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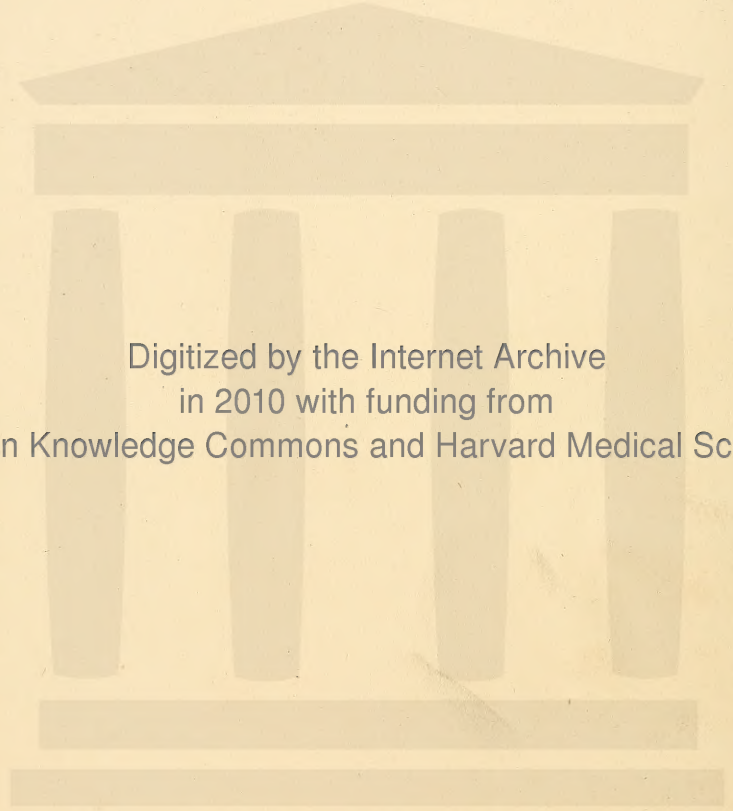

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MICRO-CHEMISTRY OF POISONS,

INCLUDING THEIR

PHYSIOLOGICAL, PATHOLOGICAL, AND LEGAL RELATIONS;

WITH

AN APPENDIX

ON THE

DETECTION AND MICROSCOPIC DISCRIMINATION OF BLOOD:

ADAPTED TO
THE USE OF THE MEDICAL JURIST, PHYSICIAN,
AND GENERAL CHEMIST.

BY

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WITH NINETY-SIX ILLUSTRATIONS UPON STEEL.

Ἀπὸ πείρης πάντα ἀνθρώποισι φιλέει γίνεσθαι.—HERODOTUS.

SECOND EDITION.

PHILADELPHIA:
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TO

My Wife,

WHO,

BY HER SKILFUL HAND,

ASSISTED SO LARGELY IN ITS PREPARATION,

This Volume

IS

AFFECTIONATELY INSCRIBED.

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PREFACE

TO

THE SECOND EDITION.

On issuing this edition of the Micro-Chemistry of Poisons, nothing need be added in regard to its scope and design to what was said in the Preface to the former edition.

The work has been thoroughly revised, and much enlarged in matter, especially by the addition of illustrative cases, largely American, and by new tests and methods of recovery of poisons from organic mixtures; and, also, by the addition of an entirely new chapter on Gelsemium poisoning, and an Appendix on the Nature, Detection, and Microscopic Discrimination of Blood.

Among other subjects added might be mentioned Poisoning by Potassium Chlorate; Post-Mortem Diffusion of Arsenic; Arsenic in Medicines, in Fabrics, and in Glass;* Dragendorff's method for the recovery of Vegetable principles; Nature of Ptomaines; and the preparation, properties, and recovery of Jervine.

The chemical nomenclature of the former edition has been entirely revised and made to conform with the more recent views of chemists on that subject.

After due consideration, it was concluded to retain the English

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* The glass of some American beakers examined since the text on this subject was in print contained 0.34 per cent. of metallic arsenic.

system of weights for indicating the behavior of given quantities of the different poisons with reagents, since this system is much more familiar to lawyers likely to consult the work, and even to most American physicians at present, than the metric system. To the professional chemist it matters little which of these systems of weights is employed for this purpose. If the reader is more familiar with metric than with English weights, he need only, after reading the fractions employed throughout the work to indicate the amount of the poison or substance present, substitute the word *solution* for the word "grain," and bear in mind that, unless otherwise stated, the reaction refers to the behavior of about 0.0648 gramme (one grain) of the solution. Thus, for $\frac{1}{100}$ grain, *read* $\frac{1}{100}$ solution.

The various solutions mentioned throughout the text are equally readily obtained by either of these systems of weights, by dissolving, by the aid of an acid or alkali if necessary, one part (grain or gramme) of the substance in one hundred parts by weight of water, when what is known as a 1–100th solution will be obtained. Ten parts of this solution mixed with ninety parts of water will constitute a 1–1000th solution. And ten parts of the last-named solution with ninety of water will form a 1–10,000th solution; that is, one part by weight of this solution will contain 1–10,000th of its weight of the substance dissolved. In like manner solutions in any other relative proportion may be prepared.

In determining the behavior of solutions of a substance with reagents, it is necessary to observe not only the degree of *dilution* of the solution, but also the *quantity* operated upon. Thus, for example, if in one instance only a single drop of a 1–100th solution is employed, whilst in another one hundred times that quantity of the solution is used, the precipitate, if any is produced, will be one hundred times greater in quantity in the latter than in the former instance, although the degree of dilution is the same in both instances. Similar results would be obtained from different quantities of like solutions of all strengths until the degree of dilution exceeded

the insolubility of the substance or compound produced or set free by the reagent, when no quantity of the solution, no matter how great, would yield any precipitate whatever. Hence, before applying reagents the solution to be tested should be concentrated as far as practicable with the application of the tests to be employed.

Two new steel Plates, including twelve illustrations of microscopic crystals, have been added to the work. These illustrations, like those of the former edition, were drawn from nature and executed upon steel by her to whom the work is inscribed. A steel Plate showing the *apparent* size of the red corpuscles of the blood of six different mammals, under a power of 1150 diameters, has also been added. These latter illustrations were drawn on steel by my daughter, Mrs. J. Marshall, and are accurate, on the steel, within at most about 1–1000th of an inch. A chromo-lithograph of Blood-Spectra and some wood-cut illustrations have also been added to the work.

The author would here acknowledge his indebtedness to Dr. Leo Mees, formerly his assistant, for much valuable assistance in collecting, mounting, and in the measurement of the corpuscles of the various bloods herein considered.

University of Pennsylvania, Philadelphia,
March, 1885.

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APPENDIX.

BLOOD.

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ILLUSTRATIONS.

CHROMO-LITHOGRAPH OF BLOOD-SPECTRA. (*Frontispiece.*)

UPON STEEL.

PLATE I.

FIG. 1. $\frac{1}{100}$ grain POTASSIUM OXIDE, as nitrate or chloride, + *Platinic Chloride.*
" 2. $\frac{1}{100}$ grain POTASSIUM OXIDE, as nitrate, + *Tartaric Acid.*
" 3. $\frac{1}{250}$ grain POTASSIUM OXIDE, as chloride, + *Sodium Tartrate.*
" 4. $\frac{1}{200}$ grain POTASSIUM OXIDE, as nitrate, + *Picric Acid.*
" 5. $\frac{1}{100}$ grain AMMONIA, as ammonium chloride, + *Picric Acid.*
" 6. $\frac{1}{25}$ grain SODIUM OXIDE, + *Picric Acid.*

PLATE II.

FIG. 1. $\frac{1}{25}$–$\frac{1}{100}$ grain SODIUM OXIDE, + *Potassium Metantimoniate.*
" 2. $\frac{1}{10}$ grain SODIUM OXIDE, + *Tartaric Acid.*
" 3. $\frac{1}{1000}$ grain SODIUM OXIDE, as chloride, + *Platinic Chloride.*
" 4. $\frac{1}{100}$ grain SULPHURIC ACID, + *Barium Chloride.*
" 5. HYDROFLUOSILICIC ACID, + *Barium Chloride.*
" 6. $\frac{1}{100}$ grain SULPHURIC ACID, + *Strontium Nitrate.*

PLATE III.

FIG. 1. $\frac{1}{100}$ grain HYDROCHLORIC ACID, + *Lead Acetate.*
" 2. $\frac{1}{1000}$ grain OXALIC ACID, on spontaneous evaporation.
" 3. $\frac{1}{1000}$ grain OXALIC ACID, + *Calcium Chloride.*
" 4. $\frac{1}{100}$ grain OXALIC ACID, + *Barium Chloride.*
" 5. $\frac{1}{100}$ grain OXALIC ACID, + *Strontium Nitrate.*
" 6. $\frac{1}{500}$ grain OXALIC ACID, + *Lead Acetate.*

PLATE IV.

FIG. 1. $\frac{1}{10000}$ grain HYDROCYANIC ACID vapor, + *Silver Nitrate.*
" 2. $\frac{1}{100000}$ grain HYDROCYANIC ACID vapor, + *Silver Nitrate.*
" 3. $\frac{1}{1000}$ grain PHOSPHORIC ACID, + *Ammonium Magnesium Sulphate.*
" 4. TARTAR EMETIC, from hot supersaturated solution.
" 5. ARSENIOUS OXIDE, sublimed.
" 6. $\frac{1}{100}$ grain ARSENIOUS OXIDE, + *Ammonium Silver Nitrate.*

PLATE V.

FIG. 1. $\frac{1}{100}$ grain ARSENIC OXIDE, + *Ammonium Magnesium Sulphate.*
" 2. CORROSIVE SUBLIMATE, sublimed.
" 3. $\frac{1}{100}$ grain LEAD, + diluted *Sulphuric Acid.*
" 4. $\frac{1}{100}$ grain LEAD, + diluted *Hydrochloric Acid.*
" 5. $\frac{1}{2500}$ grain LEAD, + *Potassium Iodide.*
" 6. $\frac{1}{1000}$ grain ZINC, + *Oxalic Acid.*

PLATE VI.

FIG. 1. $\frac{1}{100}$ grain NICOTINE, + *Platinic Chloride.*
" 2. $\frac{1}{100}$ grain NICOTINE, + *Corrosive Sublimate.*
" 3. $\frac{1}{1000}$ grain NICOTINE, + *Picric Acid.*
" 4. CONINE, pure, + vapor of *Hydrochloric Acid.*
" 5. $\frac{1}{100}$ grain CONINE, + *Picric Acid.*
" 6. $\frac{1}{100}$ grain MORPHINE, + *Potassium Hydrate.*

PLATE VII.

FIG. 1. $\frac{1}{100}$ grain MORPHINE, + *Potassium Iodide.*
" 2. $\frac{1}{100}$ grain MORPHINE, + *Potassium Chromate.*
" 3. $\frac{1}{100}$ grain MORPHINE, + *Platinic Chloride.*
" 4. $\frac{1}{100}$ grain MECONIC ACID, + *Barium Chloride.*
" 5. $\frac{1}{100}$ grain MECONIC ACID, + *Hydrochloric Acid.*
" 6. $\frac{1}{100}$ grain MECONIC ACID, + *Potassium Ferricyanide.*

PLATE VIII.

FIG. 1. $\frac{1}{100}$ grain MECONIC ACID, + *Calcium Chloride.*
" 2. $\frac{1}{1000}$ grain NARCOTINE, + *Potassium Hydrate.*
" 3. $\frac{1}{100}$ grain NARCOTINE, + *Potassium Acetate.*
" 4. $\frac{1}{100}$ grain CODEINE, + *Iodine in Potassium Iodide.*
" 5. $\frac{1}{100}$ grain CODEINE IODIDE, from alcoholic solution.
" 6. $\frac{1}{100}$ grain CODEINE, + *Potassium Sulphocyanide.*

PLATE IX.

FIG. 1. $\frac{1}{100}$ grain CODEINE, + *Potassium Dichromate.*
" 2. $\frac{1}{100}$ grain CODEINE, + *Potassium Iodide.*
" 3. $\frac{1}{1000}$ grain NARCEINE, + *Iodine in Potassium Iodide.*
" 4. $\frac{1}{500}$ grain NARCEINE, + *Potassium Dichromate.*
" 5. $\frac{1}{500}$ grain OPIANYL, + *Iodine in Potassium Iodide.*
" 6. $\frac{1}{500}$ grain OPIANYL, + *Bromine in Bromohydric Acid.*

PLATE X.

FIG. 1. $\frac{1}{100}$ grain STRYCHNINE, + *Potassium Hydrate or Ammonia.*
" 2. $\frac{1}{100}$ grain STRYCHNINE, + *Potassium Sulphocyanide.*
" 3. $\frac{1}{500}$ grain STRYCHNINE, + *Potassium Dichromate.*
" 4. $\frac{1}{2500}$ grain STRYCHNINE, + *Potassium Dichromate.*
" 5. $\frac{1}{1000}$ grain STRYCHNINE, + *Auric Chloride.*
" 6. $\frac{1}{1000}$ grain STRYCHNINE, + *Platinic Chloride.*

PLATE XI.

FIG. 1. $\frac{1}{1000}$ grain STRYCHNINE, + *Picric Acid.*
" 2. $\frac{1}{100}$ grain STRYCHNINE, + *Corrosive Sublimate.*
" 3. $\frac{1}{100}$ grain STRYCHNINE, + *Potassium Ferricyanide.*
" 4. $\frac{1}{1000}$ grain STRYCHNINE, + *Iodine in Potassium Iodide.*
" 5. $\frac{1}{100}$ grain BRUCINE, + *Potassium Hydrate or Ammonia.*
" 6. $\frac{1}{100}$ grain BRUCINE, + *Potassium Sulphocyanide.*

PLATE XII.

FIG. 1. $\frac{1}{100}$ grain BRUCINE, + *Potassium Dichromate.*
" 2. $\frac{1}{1000}$ grain BRUCINE, + *Platinic Chloride.*
" 3. $\frac{1}{100}$ grain BRUCINE, + *Potassium Ferricyanide.*
" 4. $\frac{1}{100}$ grain ATROPINE, + *Potassium Hydrate or Ammonia.*
" 5. $\frac{1}{100}$ grain ATROPINE, + *Bromine in Bromohydric Acid.*
" 6. $\frac{1}{10000}$ grain ATROPINE, + *Bromine in Bromohydric Acid.*

PLATE XIII.

FIG. 1. $\frac{1}{100}$ grain ATROPINE, + *Picric Acid.*
" 2. $\frac{1}{100}$ grain ATROPINE, + *Auric Chloride.*
" 3. $\frac{1}{100}$ grain VERATRINE, + *Auric Chloride.*
" 4. $\frac{1}{100}$ grain VERATRINE, + *Bromine in Bromohydric Acid.*
" 5. SOLANINE, from alcoholic solution.
" 6. $\frac{1}{100}$ grain SOLANINE, as sulphate, on spontaneous evaporation.

PLATE XIV.

FIG. 1. $\frac{1}{100}$ grain MORPHINE, + *Iodine in Potassium Iodide.*
" 2. $\frac{1}{1000}$ grain MORPHINE, + *Potassium Iodohydrargyrate.*
" 3. JERVINE, from ethereal solution.
" 4. $\frac{1}{100}$ grain JERVINE, + *Sulphuric Acid.*
" 5. $\frac{1}{100}$ grain JERVINE, + *Nitric Acid.*
" 6. JERVINE, from blood of cat.

PLATE XV.

FIG. 1. GELSEMINE HYDROCHLORIDE.
" 2. GELSEMIC ACID, from ethereal solution.
" 3. GELSEMIC ACID, sublimed.
" 4. $\frac{1}{1000}$ grain GELSEMIC ACID, + *Sulphuric Acid, then Ammonia*
" 5. HÆMATIN HYDROCHLORIDE.
" 6. HÆMATIN HYDROCHLORIDE, from $\frac{1}{500}$ grain of blood.

PLATE XVI.

FIG. 1. Blood-Corpuscles of Man, × 1150 diameters.
" 2. " " " Dog, × " "
" 3. " " " Mouse, × " "
" 4. " " " Ox, × " "
" 5. " " " Sheep, × " "
" 6. " " " Goat, × " "

MICRO-CHEMISTRY OF POISONS.

INTRODUCTION.

DEFINITION; APPLICATION OF THE MICROSCOPE—IMPORT OF THE TERM POISON; MODIFYING CIRCUMSTANCES—CLASSIFICATION OF POISONS —SOURCES OF EVIDENCE OF POISONING: EVIDENCE FROM SYMPTOMS—FROM POST-MORTEM APPEARANCES— FROM CHEMICAL ANALYSIS.

By the term Micro-Chemistry of Poisons, we understand the study of the chemical properties of poisons as revealed by the aid of the microscope. Although the scope of the present work is not limited to this department of the subject, yet, as that branch of the science forms a main element of the treatise, we have designated it by that title.

The instrument requisite for investigations of this kind may be comparatively simple; and but little accessory apparatus will be required. The stage of the instrument should be sufficiently large to receive a watch-glass having a diameter of not less than two inches. Object-glasses of only low power are usually required. Very often an amplification of from thirty to forty diameters will answer the purpose best, but more frequently, perhaps, a power of about seventy-five will be the most satisfactory, while in some few instances an amplification of about two hundred and fifty will be required. The objectives best suited for these powers are the inch and a half, two-thirds inch, and one-fifth inch, respectively. In these investigations, as in all others with the microscope, the lowest amplification that will reveal the true character of the object examined will be the most satisfactory. A *polarizing apparatus* will sometimes be necessary to determine the true nature of an object; and in some instances a *micrometer* will be found useful to ascertain the absolute size of the object.

In applying the microscope to the examination of the result of a chemical reagent upon a suspected solution, a single drop of the liquid, placed in a watch-glass or upon a glass slide, is treated with a very small quantity of the reagent, added by means of a pipette, and the mixture, with as little agitation as possible, transferred to the stage of the instrument. If, as is sometimes the case, the crystalline deposit produced by the reagent be readily broken up by agitation, the watch-glass containing the drop of fluid to be examined is placed on the stage of the instrument before the addition of the reagent. In many instances, as will be noticed hereafter, the formation of a precipitate is much facilitated by stirring the mixture with a glass rod. Should the mixture evolve fumes injurious to the object-glass, a flat watch-glass having a ground edge is selected, and this is covered by a piece of very thin glass. Any special directions in regard to the use of this instrument will be pointed out hereafter, as occasion may require.

A Poison is any substance which, when taken into the body and either being *absorbed* or by its *direct chemical action* upon the parts with which in contact, or when applied *externally and entering the circulation*, is capable of producing deleterious effects. There is no doubt that all poisons are to a greater or less extent absorbed into the circulation. In fact, with most of them this is certainly a condition essential to the production of their effects; yet it would appear that in the action of some substances, which produce local chemical changes, death, in some instances at least, can be referred only to the effects of the changes thus produced. The *mineral acids* and *caustic alkalies* are the principal poisons which have a direct chemical action upon the parts with which they are brought in contact. This action is due to a mutual affinity existing between the agent and the tissue. In this respect, the action of these substances differs from that of certain heated liquids, such as boiling water, which are inert at ordinary temperatures, but which, simply on account of their *condition, induce* a chemical change in the part to which they are applied, without themselves being chemically concerned in the change. When applied *externally*, some poisons are absorbed by simply being brought in contact with the unbroken skin; whilst others do not enter the circulation unless applied to an abraded or wounded surface.

Poisons differ greatly in regard to the *quantity* necessary to prove injurious. Thus, the fiftieth part of a grain of aconitine has seriously endangered the life of an adult, while, on the other hand, an ounce of

magnesium sulphate may generally be administered with impunity; yet in large quantities the latter substance has in several instances caused death, and is strictly a poison, although not commonly reputed as such. As yet we know of no substance that is poisonous in every proportion. Any of the most powerful poisons may be administered in certain quantities without producing any appreciable effect, and most of them may be so employed as to constitute valuable remedial agents.

In medico-legal inquiries, the leading idea connected with the term poison is whether the given results are directly traceable to the substance and the *intention* with which it was employed.

Poisons not only differ from each other in regard to the quantity necessary to destroy life, but the effects of the same substance may be much modified by circumstances, and even substances which to most persons are harmless may, on account of certain peculiarities of constitution, produce deleterious effects.

Causes which modify the effects of Poisons.—Among the causes which may modify the effects of poisons, may, in this connection, be mentioned Idiosyncrasy, Habit, and a Diseased State of the System.

1. *Idiosyncrasy*, or a peculiarity of constitution, may variously modify the effects of substances. Thus, in some persons ordinary medicinal doses of certain drugs, such as opium or mercury, produce violent symptoms, and even death. In other instances, substances which to most persons are harmless, and even ordinary articles of food, produce symptoms of irritant poisoning. This has been observed in the eating of certain kinds of fish, honey, pork, veal, and mutton. In still another form of idiosyncrasy, there is a diminished susceptibility to the action of certain substances which to most persons are active poisons. This peculiarity of constitution is very rare, and is most generally observed in regard to the action of mercury and opium. Dr. Christison relates an instance in which a gentleman, unaccustomed to the use of opium, took without injury nearly an ounce of good laudanum.

2. *Habit* may render certain poisons harmless in doses which to most persons would prove rapidly fatal. The influence of habit is daily seen in the use of opium, tobacco, and alcohol; and it is well known that certain other agents when administered medicinally, in frequently-repeated doses, after a time lose their ordinary effects.

Persons accustomed to the use of opium have taken daily, for long periods together, quantities of laudanum that would prove fatal to several persons unaccustomed to its use. Although this influence has principally been observed, as remarked by Dr. Christison, in regard to the action of certain organic poisons, especially such as act on the brain and nervous system, yet it seems now to be fully established that certain persons in Styria accustom themselves even to the eating of *arsenic* in doses of several grains daily, and continue the practice for many years without experiencing any of the usual effects of the poison. The statements formerly made by Dr. Tschudi and others in regard to the existence of this practice have been discredited by most writers on toxicology; but the accounts more recently published by Dr. Roscoe, as quoted by Dr. Taylor (*Med. Jur.*, Amer. ed., 1861, 693), and the direct observations of Dr. Maclagan, of Edinburgh (*Chemical News*, London, July, 1865, 36), while on a visit to Styria, seem to leave no doubt whatever of its existence. In one of the cases observed by Dr. Maclagan, the individual, a muscular young man, aged twenty-six years, swallowed, in connection with a very small piece of bread, five grains of genuine powdered arsenious oxide, or white arsenic, which he stated was about the quantity he was in the habit of taking twice a week. In the urine passed by this individual two hours afterward, as also in that passed after twenty-six hours, Dr. Maclagan detected a very notable quantity of arsenic. It is but proper to observe that the experience of most medical practitioners in the use of this substance does not accord with the results of this Styrian practice.

3. *Disease.*—In certain diseased conditions of the system, there is a diminished susceptibility to the action of certain poisons; whilst in others, there is an increased susceptibility, even to the action of the same substance. Thus, in tetanus, hydrophobia, mania, and delirium tremens, quantities of opium which in ordinary states of the system would be fatal may often be administered with beneficial effects. In a case of tetanus related by Dr. Watson (*Practice of Physic*), something over four ounces of laudanum was taken on an average daily, for twenty days; after which the patient recovered. The same writer quotes another instance of the same affection, in which an ounce of solid opium was taken, in divided doses, daily, for twenty-two days. So also, in inflammation of the lungs, enormous doses of tartar emetic have been given with advantage. On the

other hand, in cases in which there is a predisposition to apoplexy, an ordinary dose of opium may cause death. In like manner, in certain diseases, there is an increased susceptibility to the action of mercury and other mineral substances.

CLASSIFICATION OF POISONS.—Poisons may be arranged, according to the symptoms they produce, under three classes,—namely, IRRITANTS, NARCOTICS, and NARCOTICO-IRRITANTS. Since, however, there are many poisons the effects of which are subject to great variation, and others which according to their ordinary effects might with equal propriety be placed in one or another of these classes, this classification is open to much objection.

IRRITANT POISONS, as a class, produce irritation and inflammation of the stomach and bowels, attended or followed by intense pain in these parts, tenderness of the abdomen, and violent vomiting and purging, the matters evacuated being often tinged with blood. Some of the members of this class, such as the mineral acids and caustic alkalies, also possess corrosive properties, and accordingly occasion, in addition to the effects just mentioned, more or less disorganization of the mouth, throat, œsophagus, and stomach. The action of these substances, if not too dilute, is immediate, and is attended with a sense of burning heat in the parts with which they come in contact. When highly diluted, any of the corrosive poisons may act by simply inducing irritation and inflammation.

The irritant poisons may be divided into three sections, according to the kingdom of nature to which they belong,—namely, *mineral*, *vegetable*, and *animal*. The first section is much the largest, and embraces, with the exception of some gaseous substances, all strictly inorganic poisons. Gamboge and cantharides are, respectively, examples of the second and third sections.

NARCOTIC or CEREBRAL POISONS are such as act principally on the brain and spinal marrow, more especially on the former. They induce headache, vertigo, stupor, impaired vision, delirium, insensibility, paralysis, convulsions, and coma. This class contains comparatively few substances, the principal of which are opium and hydrocyanic acid. Several of the poisonous gases belong to this class.

NARCOTICO-IRRITANTS partake, as indicated by their name, of the action of both the preceding classes. Thus, they may produce, as a result of their irritant action, nausea, pain in the stomach,

vomiting, and purging; and as a result of their action on the nervous system, stupor, delirium, paralysis, coma, and convulsions. Some of them, however, do not usually produce well-marked symptoms of irritation; and all of them produce their most marked effects on the nervous system. A few, such as strychnine and brucine, act chiefly on the spinal cord, and produce violent tetanic convulsions, without any other prominent symptom. Hence these have been termed the *Convulsives* or *Spinal* poisons. All the members of this general class, which is quite numerous, are derived from the vegetable kingdom.

In referring the symptoms in a given case to the action of either of the above classes, it must not be forgotten, as already intimated, that the members of each do not always produce the same effects. Thus, arsenic has occasioned symptoms similar to those of narcotic poisoning; whilst opium has produced effects resembling poisoning by an irritant.

Sources of Evidence of Poisoning.

The medical evidence in cases of poisoning is derived chiefly from—1. *The symptoms;* 2. *The post-mortem appearances;* and, 3. *Chemical analysis.*

1. *Evidence from the Symptoms.*

In forming an opinion in a case of suspected poisoning, the medical examiner should acquaint himself with not only the special character of the symptoms present, but also, as far as practicable, the previous health and habits of the patient, when food or drink was last taken, whether in taking it any peculiar taste or odor was observed, and whether others partook of the same food.

Among the characters of the symptoms of poisoning usually mentioned by writers on this subject, the most constant are—1. The symptoms arise suddenly, and soon after the taking of food, drink, or medicine; and, 2. They rapidly prove fatal.

1. *The symptoms occur suddenly, and soon after the taking of some solid or liquid.*—The greater number of poisons, when taken in fatal quantity, manifest their action either immediately or within a short period, the symptoms of but few being delayed, under ordinary circumstances, much beyond an hour. Many instances might be cited in which a knowledge of the time that elapsed between the taking of food or drink and the appearance of the suspected symp-

toms was in itself sufficient to determine that they were really due to natural causes and not to the effects of poison. In considering this relation, however, it must not be overlooked that the interval between the taking of a poison and the first appearance of symptoms not only varies with each substance, but the time, as well as the character of the symptoms of the same poison, may be more or less affected by circumstances, such as quantity, the state in which administered, condition of the stomach, combination with other substances, and, as already mentioned, a diseased state of the system. Thus, strychnine, when taken in fatal quantity, has produced violent symptoms within five minutes afterward, and they usually appear within thirty minutes; yet they have been delayed, in one instance at least, for three hours. It is well known that antimony, arsenic, lead, and various other poisons, when taken into the system in repeated small doses, may give rise to effects wholly different from those usually produced by a single poisonous dose of the substance.

As a general rule, poisons act more speedily when taken in the state of solution than in the solid form. On the other hand, a full stomach, and, according to Dr. Christison, sleep, may delay the action of certain substances. That the action of one poison may be modified by the presence of another, is well illustrated by the following case. A man, aged twenty-nine years, swallowed three grains of strychnine, one drachm of opium, and an indefinite quantity of quinine. When seen by a physician *twelve* hours afterward, he only complained of feeling "queer." But there was extreme cerebral excitement; the pulse quick, full and strong; pupils contracted; the whole face of a deep-red color; tongue tremulous and covered with a brownish-white fur; surface of the body hot, with profuse perspiration; body and limbs in violent tremor, and at intervals spasmodic action of all the muscles, alternating with comparative quiet and drowsiness, from which he was easily roused. Upon the administration of full emetic doses of zinc sulphate, opium was freely ejected. One hour later, the patient became quite drowsy, but when roused would start violently and remain delirious for some minutes. In two hours more, complete stupor suddenly supervened, and continued, with but little change, till death, which occurred forty hours after the mixture had been taken. (*Chicago Medical Journal*, November, 1860.) How far the first appearance and character of the symptoms of a particular poison *may* depart from their ordinary course, can be

learned only from a comparison of well-authenticated cases. In this respect, our knowledge at present in regard to the effects of very many substances is extremely limited, and there is no reason to believe that in regard to any we have as yet met with the greatest deviation possible.

In this connection, it must also be borne in mind that there are certain natural diseases, the symptoms of which resemble more or less those of poisoning, and which may appear suddenly at any time. In fact, some of these diseases, such as apoplexy and perforation of the stomach, are more likely to occur soon after the taking of food than at any other period. Instances of this kind, however, are of rare occurrence, and the subsequent history of the case will usually enable the practitioner to determine without difficulty its true nature. Nevertheless, cases have occurred, the nature of which could be established only by the post-mortem appearances and chemical analysis.

When two or more persons who have eaten of the same food are suddenly seized with violent symptoms, there is, of course, increased reason for suspecting the presence of a poison. This circumstance has in some instances at once revealed the source of the poison. Results of this kind, however, may be due to an unwholesome or diseased condition of the food; or to its having accidentally become contaminated with a poisonous metal, such as copper, lead, or zinc, during its preparation. On the other hand, several persons may partake of the same meal, or even of the same food, and poison have been designedly introduced only into the portion intended for a particular individual. Thus, in a case in which we were consulted, and which will be referred to hereafter, a family of several persons having mush and milk for supper, the mush was placed on the table in one dish, while the milk was distributed at the usual places of sitting, in bowls. Into one of the bowls strychnine had been introduced, and its intensely bitter taste was, perhaps, the only circumstance that saved the life of the person for whom it was intended; only, however, to become the victim a few days afterward of a fatal quantity, under a form in which its taste was entirely concealed. In another instance, the plum-pie served for dinner was furnished to the several members of the family, on separate plates; under the crust of one of the pieces, arsenic had been placed, and proved fatal to the person who ate it. From what has already been stated, it is obvious that several persons may even partake of the same poisoned

food, and the results be very different. Dr. Beck quotes several striking examples of this kind.

Lastly, in inquiries of this kind it must be remembered that poisons may be introduced into the system in other ways than with food, drink, or medicine. Thus, poisoning by the external application of the substance is not of unfrequent occurrence; the same is also true of the inhalation of certain vapors and gases. Instances of this kind, however, are usually the result of accident. Several instances are recorded, in which poisons were criminally introduced into the rectum and vagina; and Dr. Christison cites a case in which a fatal quantity of sulphuric acid was poured into the mouth of an individual while asleep.

2. *The symptoms rapidly run their course.*—The duration of the symptoms of poisoning, like their appearance, is subject to great variation, even with regard to the same substance. Some few poisons, as hydrocyanic acid, nicotine, and conine, usually prove fatal within a few minutes, and most of them within comparatively short periods. Yet, as just intimated, great differences have been observed even in regard to the action of the same substance. Thus, the fatal period of hydrocyanic acid poisoning has been protracted for several hours; whilst, on the other hand, arsenic, which on an average perhaps does not prove fatal in less than twenty-four hours, has caused death in less than two hours. As a general result, a large dose of a given substance will prove more rapidly fatal than a small one, yet this is by no means always the case. Half a grain of strychnine has caused the death of an adult in less than twenty minutes, while in a case in which between five and six grains were taken, death was delayed for six hours; and even larger quantities than the last mentioned have been followed by recovery.

The vegetable poisons as a class, usually, either prove fatal within at most a very few days, or the patient entirely recovers; but many of the mineral substances frequently do not cause death until after the lapse of several days. In fact, many of the members of the latter class may give rise to secondary effects which may extend through an interval of many weeks, or even months. The usual period within which each of the more common poisons proves fatal, and how far it has departed from its ordinary course, will be pointed out hereafter in the special consideration of the individual substances.

In considering the duration of the symptoms in a case of suspected

poisoning, it must be remembered that the symptoms of some natural diseases not only closely resemble those of certain kinds of poisoning, but also run their course with equal rapidity. In most instances, however, a careful examination of the symptoms, with a full history of the case, when this can be obtained, will enable the medical practitioner to form a correct diagnosis; but cases not unfrequently occur the true nature of which can be established only by the post-mortem appearances and chemical analysis.

The diseases most likely to give rise to symptoms resembling *irritant* poisoning are, cholera, inflammation of the stomach and bowels, and perforation of the stomach; and those that may simulate *narcotic* poisoning—apoplexy, inflammation of the brain, and organic diseases of the heart. Cholera has been mistaken for poisoning by arsenic, and, on the other hand, arsenical poisoning has been mistaken for that disease. The same has also been true in regard to apoplexy and opium poisoning. The symptoms of disease of the heart, in the rapidity of their action, may closely resemble the effects of hydrocyanic acid and of nicotine. The true nature of some of the foregoing diseases is readily revealed upon dissection; but others, like the poisons with whose symptoms they may be confounded, leave no well-marked morbid appearances.

In the examination of a case of suspected poisoning, the medical attendant should obtain as far as possible a full history of the progress of the symptoms and their relation to the taking of food, drink, or medicine. All suspicious articles of this kind should be collected; and if vomiting has occurred, the matters ejected should also be collected and their character noted. All articles thus obtained should be carefully sealed, if solid, in clean white paper, and if liquid, in clean glass jars, distinctly labelled, and preserved for future examination, the collector being careful not to permit any such article to pass out of his possession until delivered to the proper person.

A chemical examination of some of these articles may at once reveal the true nature of the symptoms. It need hardly be remarked that a failure to discover poison under these circumstances will by no means be conclusive evidence that a poison had not been taken. On the other hand, the detection of poison in a remnant of food or medicine taken by the person will not of itself be conclusive proof that a poison had been taken. Symptoms of poisoning have been feigned and poison put into articles of this kind for the purpose of

charging another with an attempt to murder. The existence of this fact can, of course, be determined only by the attending circumstances. Some years since we were engaged in a case in which it clearly appeared that a man maliciously put a large quantity of white arsenic into an alcoholic medicine he was using, and actually swallowed sufficient of the mixture to produce serious symptoms; he then charged his wife with the poisoning.

2. *Evidence from Post-mortem Appearances.*

There are very few instances in which the post-mortem appearances are peculiar to poisoning. Nevertheless, this part of the evidence should always be very carefully considered, for when taken in connection with the symptoms and other circumstances, it may fully establish the true character of a case which would otherwise be doubtful. In death from natural disease, a post-mortem examination may at once discover the fact. However, appearances of ordinary disease may be present, and death have resulted from the effects of poison. Several instances, in which coincidences of this kind existed, might be cited. The presence of some few poisons, as opium and hydrocyanic acid, may sometimes be recognized by their odor; and others, when in the stomach, by their color or botanical characters. It is a popular belief that great lividity of the body and rapid decomposition always attend and are characteristic of death from poisoning; but these results are rarely produced, and are by no means peculiar.

Some poisons leave no appreciable morbid changes in the dead body; and of those that usually do, the appearances are subject to great variety, and in many instances similar to the effects of ordinary disease, or even the results of cadaveric changes. The mineral acids and caustic alkalies usually leave the most marked evidence of their action, and in some instances this is quite characteristic.

The *irritant* poisons as a class usually produce irritation and inflammation of one or more portions of the alimentary canal, the effects being sometimes confined to the stomach, while at other times they extend to a greater or less degree throughout the entire canal. In some instances the coats of the stomach become ulcerated and softened, and even perforated. Poisons of this class, however, may cause death without leaving any discoverable change in the body. This has been the case even in respect to some of the more acrid and

corrosive substances. In several instances of poisoning by arsenic, which generally produces strongly marked appearances in the stomach and bowels, nothing abnormal was found upon dissection. In the minute examination of the tissues of the alimentary canal, M. Baillou advises the inspection to be made under transmitted light.

Narcotic poisons in some instances produce more or less distention of the veins of the brain, but in others they leave no marked morbid appearances, and in none are the appearances peculiar. According to Orfila, the lungs almost always present livid and black spots, and their texture is more dense and less crepitant. These appearances, however, may result from ordinary causes. In some few instances there has been more or less irritation of the alimentary canal; but this condition was most probably induced by the vehicle in which the poison was taken, or by the remedies subsequently administered.

Narcotico-irritants partake in the nature of their effects of both the preceding classes. Thus, they may produce irritation and even ulceration of portions of the alimentary canal, and congestion of the lungs and of the veins of the brain and its membranes. But in most instances the morbid changes are not well marked.

The usual morbid changes produced by the individual poisons will be pointed out hereafter; but in this connection may be briefly mentioned some of the appearances which may be equally produced by ordinary disease or cadaveric changes and by poisoning.

Appearances common to Poisoning and Disease.—Redness of the stomach and intestines as the effect of poisoning, cannot in itself be distinguished from that arising from natural disease. This condition is not only frequently the result of active disease, but it has often been observed immediately after death in cases in which during life there were no indications of derangement of the stomach or bowels. Moreover, various pathologists have observed that pseudo-morbid redness of the mucous membrane of the stomach sometimes makes its appearance several hours after death. Dr. Christison is of the opinion that an effusion under the villous coat of the stomach, and incorporation with its substance, of dark brownish-black blood, is characteristic of violent irritation, if not of the effects of poison alone. It is well known that colored substances within the stomach, and the contact of this organ after death with the adjacent parts, may cause it to become more or less colored. But these appearances are readily distinguished from the effects of poison.

Softening of the stomach is another appearance which may give rise to embarrassment. When due to the action of poison, it is usually accompanied by other appearances which readily distinguish it from the effects of ordinary disease or post-mortem changes. Dr. Carswell has shown that this condition is not unfrequently produced by the chemical action of the gastric juice after death. He also observes that in softening of the mucous membrane of the stomach as the result of inflammatory action, the tissue is always more or less opaque, and the action attended by one or more of the products of this pathological state; whereas in post-mortem softening, the tissue is always transparent, and the action never attended with serous effusion or other concomitants of inflammation.

Ulceration and *perforation* of the stomach are not unfrequently produced by corrosive poisons, but they, especially the latter, are rarely met with as the result of the action of the simple irritants. As the effect of natural disease or post-mortem action, they are not uncommon. In many instances these appearances, as the result of poisoning, can be distinguished from those arising from other causes only by a history of the symptoms during life, or by the detection of poison in the tissues or other parts of the body. This distinction is usually well marked in the action of the mineral acids and caustic alkalies.

Perforation of the stomach has not unfrequently occurred from gelatinization of its tissues, and in cases in which during life there was no evidence of a diseased state of that organ. These appearances have been chiefly observed in cases of violent or sudden death. It was formerly believed that this condition was always a morbid process, and characteristic of a special disease. But, since the researches of modern pathologists have shown that the gastric juice has the property of dissolving the dead stomach, and that many of these lesions have undoubtedly been due to the action of that fluid after death, there is little doubt that they may all be referred to post-mortem changes. When the gastric juice escapes through the aperture thus produced, it may, as has often been the case, exert its solvent action upon the adjacent organs. As these appearances are unattended by signs of irritation, they are usually readily distinguished from the effects of poisoning. Should, however, a perforation of this kind occur in a case in which prior to death the stomach was affected with signs of irritation, it might be impossible

from the appearances alone to determine the true character of the perforation.

Perforation of the œsophagus and of the intestines, as the result of poisoning, is not at all likely to occur. In fact, there seems to be only one instance of the former, and none of the latter, on record. But these conditions, as the result of disease, have often been observed; and they have even resulted from the action of the gastric juice after death.

Points to be observed in post-mortem examinations.—All investigations of this kind should be made in the presence of the proper law officer; and it is well for the examiner to have the assistance and corroboration of another physician. All appearances observed, whether abnormal or otherwise, should be fully written down at the time of their observance. The length of time the person has been dead; how long he survived the first symptoms; and the condition of the body in respect to external appearances, should as far as practicable be learned and carefully noted. In the dissections, the condition of the entire alimentary canal, and of all the organs essential to life, should be minutely examined; in the female, the vagina and uterus should also be inspected. The stomach with its contents, and a portion of the small intestines, properly ligatured, should be removed from the body. The condition of these organs, and the nature of their contents, may then be examined. In some instances, however, it is best not to open these organs until they are delivered to the chemist. A portion of the liver and of the blood should also be removed for chemical analysis. And in some instances it is important to remove other parts of the body, as the kidneys, spleen, heart, and brain, and even portions of the muscles, for chemical examination.

All the organs and the blood thus removed should be collected in *separate*, clean glass vessels, great care being taken that none of the reserved substances at any time be brought in contact with any substance that might afterward give rise to suspicion. Before passing out of the sight of the examiner, the bottles should be securely sealed and fully labelled. They should then be retained in his sole possession until delivered to the proper person.

3. *Evidence from Chemical Analysis.*

Importance of chemical evidence.—In most charges of poisoning, the final issue depends upon the results of the chemical analysis. In fact, in many instances in which the evidence from symptoms, post-mortem appearances, and moral circumstances is very equivocal or in part wanting, a chemical examination may at once determine the true cause of death. It must be remembered, however, that a person may die from the effects of poison and not a trace of its presence be discoverable in any part of the body; while, on the other hand, the mere discovery of a poison in the food or drink taken or in the body after death, is not in itself positive proof that it occasioned death.

It has been claimed that a failure to detect poison in the dead body, by proper chemical skill, was evidence that death was the result of some other cause; but this claim is entirely groundless. The symptoms and pathological appearances, at least in connection with moral circumstances, are often sufficient in themselves fully to establish death from poisoning; and a number of convictions have very properly been based on these grounds in instances in which chemical evidence was wanting, and even when it had entirely failed. There are a number of organic poisons which at present cannot be recognized by chemical tests; and instances are recorded in which death resulted from large quantities of some of the poisons most easy of detection, and not a trace could be discovered in any part of the body. It is obvious that the discovery of minute traces of such poisons as are used medicinally could not, independently of symptoms and other circumstances, be regarded as evidence of poisoning.

Substances requiring analysis.—The substances that may directly become the subject of a chemical analysis, in a case of suspected poisoning, are: the pure poison in its solid or liquid state; suspected articles of food or medicine; matters ejected from the body by vomiting or purging; the urine; suspected solids found in the stomach or intestines after death; the contents of the stomach or bowels; any of the soft organs of the body, as the liver, spleen, etc.; and the blood.

Sometimes it is only necessary to examine one of the above-mentioned substances; but in many instances two or more of them

require examination. If a poison be thus detected, it will sometimes become necessary to examine substances other than those specified, in order to determine its real source. The evidence of poisoning is, of course, most complete when the poison is recovered from some of the soft organs of the body, after it had been absorbed. So, also, the proof will be more direct when the poison is detected in the contents of the stomach or intestines, than in articles of food or medicine.

Precautions in regard to analyses.—When called to make a chemical examination of any suspected material, the analyst should obtain, as far as practicable, a knowledge of the symptoms, and, if death has taken place, of the post-mortem appearances, observed in the suspected case: since these, when known, will generally enable him to decide at least to which class of poisons the substance belongs, and in some instances will even indicate with considerable certainty the individual substance. He may thus, by following these indications in the analysis, save much labor, and—which in many instances is of much more importance—be enabled fully to establish the presence of poison when present in quantity too minute to be recognized under other circumstances. It must not be forgotten, however, that irritant poisons have produced symptoms resembling those induced by some of the narcotics, and that the latter may produce symptoms of irritant poisoning.

So, also, before applying any chemical test to a suspected solid or liquid, its quantity—of the former by weight, and of the latter by measure—should be accurately determined. In the application of the reagents, the very least quantity of the material that will answer the purpose should, at least at first, be employed for each test. In like manner, in the preparation of complex mixtures, the residual solution should be reduced to the very smallest volume compatible with the application of the tests that it may become necessary to apply. There is little doubt that in many of the reported instances of non-detection of poisons the failures have resulted from a neglect of this point. It should always be borne in mind that a given quantity of a poison, when in solution in a small quantity of fluid, may yield, with a given reagent, perfectly characteristic results, whereas if the solution be but slightly more dilute, the reaction may entirely fail. Thus, the hundredth part of a grain of nicotine in one grain of water yields with platinic chloride a copious and rather

characteristic crystalline precipitate, while the same quantity in ten grains of that liquid yields no precipitate whatever.

In the preparation of the contents of the stomach and of the solid organs of the body, it is often advisable to employ only about one-half or two-thirds of the matter for the first examination. This proportion will perhaps in all cases, at least in regard to mineral poisons, suffice to show the poison if present, while in case of accident the analysis could be repeated. When, however, the analyst has perfect confidence in his ability to go safely through with the examination, it is perhaps best not to make this division of matter, at least in the investigation for certain organic poisons. The minute quantity of poison usually taken up by the blood, especially in the case of the alkaloids, renders it necessary to operate upon comparatively large quantities of this fluid, and to conduct the examination with extreme care.

When the symptoms or attending circumstances do not point to a particular poison, or at least to the class to which it belongs, it is obvious that a division of the matter submitted for examination becomes absolutely necessary. Under these circumstances, great care should be exercised not to subject the matter to any process that would preclude the possibility of examining for any poison for which it might afterward become necessary to look.

It need hardly be observed that during investigations of this kind the examiner should never lose sight of the suspected material, except when it is in some secure place; and the greatest possible care should be taken that it is not brought in contact with any substance the nature of which is not fully understood. A neglect of these directions may prove fatal to the results of a chemical examination. The careful analyst need not be cautioned against hasty conclusions in regard to the results of reagents.

After the presence of a poison is fully established, it is in most instances only necessary to be able to state the probable amount present; but sometimes it is necessary to determine its exact quantity. In all cases in which it is practicable, it is best to determine the actual amount recovered; but it not unfrequently occurs, especially in the detection of absorbed poison, that the quantity present is so small as not to admit of a direct quantitative analysis. Under these circumstances, we may often, by accurately noting the volume of solution obtained and observing the comparative reaction of several

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tests, estimate very closely the strength of the solution, and from this deduce within narrow limits the amount of the poison present.

It was formerly claimed that unless a quantity of poison sufficient to destroy life was found in the dead body, the chemical evidence of poisoning was defective. But it is now a well-known fact that a person may die from the effects of a large dose, and very little or even not a trace of the noxious agent remain in the body at the time of death. As any of the poison remaining in its free state in the stomach at the time of death had no part in producing the fatal result, it is obvious that to recover a fatal quantity from that which had been absorbed, and which was really the cause of death, even granting that none had been eliminated from the body with the excretions, would require an analysis of the entire body and the recovery of every portion of the poison from the complex mass,—the first of which is impracticable and the second impossible. It is only, therefore, in cases in which more than a fatal dose remains in the body at death that we are able to recover sufficient to destroy life. Moreover, as already stated, the amount of poison in the body at the time of death is in itself no index whatever of the actual quantity taken.

Value of individual chemical Tests.—The result of a chemical examination will depend, at least in great measure, upon how far we are acquainted with reactions peculiar to the substance under consideration; the delicacy of these reactions; and, in many instances, our ability to separate the substance from foreign matter. There is usually no difficulty in recognizing the presence of any of the mineral poisons, even when present only in minute quantity; but the case is very different in regard to the detection of many of the organic poisons. For the recognition of many poisons we are at present familiar with several tests, the reaction of each of which is characteristic of the substance; while for the detection of others we are acquainted with only one such reaction; there are others still for which we have no specific reagent, but whose presence can be fully established by the concurrent result of several tests; lastly, there are some organic poisons for the detection of which, at present, there is not known even any combination of chemical reactions by which their presence can be determined. Some of the poisons of the last-mentioned class may, in the form of leaves, seeds, or roots, be recognized by their botanical characters; and others, by their peculiar

physiological effects, especially when these are taken in connection with some of their general chemical properties. Among the poisons that can be readily detected when in their pure state, there are some which when present, even in quite notable quantity, in complex organic mixtures, adhere so tenaciously to the foreign organic matter that it is difficult or impossible to separate them in a state sufficiently pure to determine their presence.

For the detection of all the poisons considered in the present volume, with the exception of aconitine, we are acquainted, under certain conditions, with one or more special chemical reactions; and most of them, especially by the aid of the microscope, can now be recognized with absolute certainty, and separated from complex organic mixtures, even when present only in exceedingly minute quantity. Thus, at present we can recognize by chemical means, when in its *pure* state, the presence of the 1–10,000th of a grain, and in some instances even less, of either arsenic, mercury, strychnine, or hydrocyanic acid, with absolute certainty. It does not, however, follow that quantities as small as these when present in complex mixtures can be recovered and their nature then established. It is a popular idea, and indeed a very fair inference from the statements of some writers, that the quantity of a substance that can be recognized by chemical means in its pure state represents that which can be detected under all circumstances. But this is a great error, since the quantity that can thus be recognized, and the amount necessary to be present in a complex mixture to enable us to separate that quantity, may differ many hundreds and even thousands of times: the difference usually being in proportion to the complexity of the mixture.

From what has already been stated, it is obvious that in determining the nature of a suspected substance it is not enough that it yields affirmative reactions with a given number of reagents; but we must know that one or more of these taken singly, or two or more of them taken in connection, are peculiar to the substance. Thus, aconitine can be precipitated by several different reagents, yet none of these reactions taken singly nor several of them taken in connection, when obtained from small quantities of organic mixtures, will fully establish the presence of this alkaloid, since there are many other organic substances which yield similar results. We have, however, for the detection of this poison, a delicate and characteristic test in its peculiar physiological effects. Again, morphine yields certain results with

several different reagents, yet neither of these taken singly, when obtained from small quantities of amorphous organic mixtures, is characteristic of this poison; but the concurrent action of two or more of them may fully establish its presence, since there is no other substance known that possesses these several properties in commom with morphine. When, however, we have even only a very minute quantity of this poison in its crystalline state, then one or more of these tests taken singly may be characteristic, since most of the fallacious substances are uncrystallizable. It frequently happens that a test of this kind is applied under conditions in which the substance having reactions similar to that of the suspected substance could not be present, when, of course, an affirmative reaction is specific.

The true nature of a reaction that is common to several substances can in some instances be readily determined by means of the microscope. Thus, a solution of silver nitrate, when exposed separately to several different vapors, becomes covered with a white film; but hydrocyanic acid is the only one in the action of which the film is *crystalline*, and this is characteristic even with the reaction of the 1–100,000th of a grain of the acid. A substance may yield a peculiar crystalline precipitate at one degree of dilution, while at another the precipitate may not be characteristic, as illustrated in the action of bromine with atropine, which yields from one grain of a 1–20,000th or stronger pure solution a specific crystalline deposit, while from solutions but little more dilute the result is not peculiar.

So, also, the true nature of a reaction may in some instances be determined by submitting the result to a subsequent test. A slip of clean copper, when boiled in a hydrochloric acid solution of either arsenic, mercury, antimony, or of several other metals, becomes coated with the metal; but when the coated copper is heated in a reduction-tube, arsenic is the only substance that will yield a sublimate of octahedral crystals, and mercury the only one that will furnish metallic globules. Some tests can be successfully applied only to comparatively pure solutions, whilst others can be thus applied to very complex mixtures. The copper test for arsenic and mercury, just mentioned, yields in many instances much the same results in complex mixtures as with pure solutions. But this result is true only in regard to a few tests, and these for the detection of mineral substances.

In examining a suspected substance or solution, it is usually best, especially when the quantity of material is limited, to begin with the most characteristic test, after which, if it produces an affirmative result, one or more corroborative tests should be employed. In many instances the positive reaction of a single test, obtained from even a very small fractional part of a grain of the poison, may, in a chemical point of view, be as conclusive of its presence as the result of any number of tests applied to any quantity of the substance however great. Yet, for medico-legal purposes, it is always best, if sufficient material be at hand, to confirm the results by several tests, and, when practicable, show the presence of the poison by two or more independent methods.

If any of the corroborative tests thus applied should fail, we should be able to account for the failure. This may be due to want of delicacy on the part of the reagent, or to the presence of some substance, such as a free acid, an alkali, or other foreign matter, which prevents its normal action. For the same reason, if the test first applied should fail, we should be cautious in concluding the entire absence of poison, unless we are fully acquainted with the conditions under which the test was applied. Thus, it has just been stated that copper becomes coated with arsenic when heated in a mixture of this metal and hydrochloric acid, but we may have an impure mixture of this kind in which the arsenic will not be deposited, even when present in large quantity. In fact, there is no test that will produce with a given substance the same results under all conditions. In the special consideration of the individual tests, the conditions under which they may fail, as well as the *fallacies* to which they are liable, and the *limit* of each for pure solutions, will, as far as practicable, be pointed out.

The behavior of a test the reaction of which taken alone has no positive value, is often important in directing the application of other tests. A solution of iodine produces a distinct reaction even with the 1–100,000th of a grain of strychnine, when in solution in one grain of water; yet, as this reaction is common to most of the alkaloids and other organic substances, the mere production of a precipitate would not establish the presence of the alkaloid in question. Should, however, this test under proper conditions fail, it would follow that the suspected solution did not contain even the 1–100,000th of its weight of the alkaloid, and therefore that it would be useless to apply any less delicate test for this poison to the solution.

Failure to detect a poison.—Numerous instances are reported in which persons died from the effects of poison and none was discovered by chemical analysis in the body after death. This result has most frequently been observed in poisoning with organic substances, but it has happened when mineral poisons, and even those which are most easily detected by chemical tests, had been taken in large quantity.

A failure of this kind may be due to any of the following circumstances: 1. The poison may have been one of the organic poisons which cannot at present be recognized by chemical tests. 2. The quantity present in the part examined may have been so minute as under the circumstances not to admit of recovery, or at least in a state sufficiently pure to permit its true nature to be established. 3. The poison may have been removed from the stomach and intestines by vomiting and purging or by absorption. 4. The absorbed poison may have been carried out of the system with the excretions. 5. If volatile, like hydrocyanic acid and some few other poisons, it may have been dissipated in the form of vapor. 6. It may have undergone a chemical change in the living body, or, especially if of organic origin, have been decomposed in the dead body if far advanced in putrefaction.

The period in which a poison may be entirely expelled from the stomach by *vomiting* is subject to great variation. Dr. Christison cites two instances of poisoning by arsenic in which death ensued under much vomiting in five hours, and in one of which none of the poison could be detected either in the contents or tissue of the stomach, and in the other only the fifteenth part of a grain was recovered. In two other instances of like poisoning, in which death took place in eight hours, after one ounce and nearly two ounces respectively had been taken, not a trace of the noxious agent was discovered in the stomach. On the other hand, Orfila mentions a case in which arsenic was detected in the contents of the stomach of an individual who had vomited almost incessantly for two entire days. And in a case which we examined some years since, in which there had been almost incessant vomiting for thirty-two hours, *forty-two grains* of arsenic were recovered; it having been taken in the form of "fly-powder," and much of it existing in the solid state attached to the mucous membrane of the organ. In a case examined by Prof. S. A. Lattimore, of Rochester, N.Y., one hundred and three grains of

arsenic were found in the stomach of a woman who died from the effects of the poison. How long the woman survived after taking the poison in this case is not known.

Similar results have been observed in regard to the removal of poison from the stomach and bowels by *absorption*, even in cases in which there was neither vomiting nor purging. Comparatively large quantities of some of the organic poisons have apparently thus disappeared within a very few hours. In a case of poisoning by strychnine, in which about six grains had been taken and death ensued in six hours, repeated analyses, by Dr. Reese, of Philadelphia, of the contents of the stomach and of a portion of the small intestines, made eight weeks after death, failed to reveal the presence of a trace of the poison. So also, in a case of poisoning by not less than two ounces of laudanum, Dr. Christison failed to detect morphine in the contents of the stomach, although the person survived the taking of the poison only five hours. Some of the mineral poisons may remain in the contents of the living stomach and intestines for several days. Thus, Dr. Geoghegan found arsenic in the contents of the colon after twelve days.

After a poison has been absorbed and carried into the tissues of the body, it is sooner or later *eliminated* from the body with the different excretions, more especially with the urine. Many instances are recorded in which death took place with the usual rapidity from the effects of large doses of the most easily detected mineral poisons, and there was a failure to discover the poison in any part of the body. Orfila concluded from his investigations that arsenic, mercury, and the mineral poisons generally were under ordinary circumstances entirely eliminated from the living system in about fifteen days, and this view has been sustained by the observations of others. The period of entire elimination, however, is subject to considerable variation: it has been limited to a few days, while, on the other hand, some of the mineral poisons have been detected in the urine even several weeks after they were taken into the stomach. Thus, arsenic has been found in the fæces passed two weeks, and in the urine voided *six weeks*, after the metal had been taken, and copper has been present in the liver even *three months* after being administered in divided doses.

There is no longer any doubt whatever that the vegetable poisons, such as the alkaloids, enter the blood by absorption, in part

at least, in their unchanged state, and are thus conveyed to the tissues; but there has not unfrequently been a failure to recover them from the blood and tissues, even under apparently the most favorable circumstances. We have recovered all the poisons of this class considered in the present treatise from the blood of poisoned animals, but that they should always be recovered, even under favorable conditions, from the blood of the poisoned human subject, we will not pretend to assert; still, with improved methods of analysis and the aid of the microscope, there is little doubt that failures of this kind will become less frequent.

In regard to the effects of *chemical changes* and *decomposition* in removing poison beyond the reach of analysis, it may be remarked that some of the organic poisons, especially when of a volatile nature, may undergo a change of this kind in the dead body after very short periods. In a case of suicide by *hydrocyanic acid*, quoted by Professor Casper, no trace of it was found in the stomach twenty-six hours after death, but there was present a considerable quantity of *formic acid*, as the result of the metamorphosis of the original poison. In like manner, *hydrocyanic acid* may be converted into *sulphocyanic acid* during the process of putrefaction. So also, phosphorus, by combining with oxygen, is sooner or later converted into one or more of the acid oxides of phosphorus; this conversion may even be completed in the living body. It need hardly be remarked that when a chemical antidote has been administered, none of the poison may remain in its uncombined state, or in the form in which originally taken, in the stomach.

On the other hand, some of the vegetable alkaloids *may* remain in their unchanged state in the dead body and other decomposing organic mixtures for at least some months. Although the metallic poisons may undergo chemical changes, even in the living body, yet, as the metals themselves are indestructible, the compounds thus produced may in some instances be recovered even after many years.

Of chemical reagents.—Only those having practical experience in the matter know the difficulty of obtaining at least certain reagents and chemicals in a state of absolute purity. The impurity may in some instances be an ordinary poison, and even consist of the very substance suspected to be present in the matters submitted for examination; while in others it may be of a nature that will very much modify or altogether prevent the normal reaction of the

reagent, or give rise to results which may readily be attributed to some other cause. Thus, in one of the methods for the detection of arsenic, the principal chemicals employed are sulphuric acid and zinc, yet arsenic is not unfrequently present as an impurity in each of these chemicals. Impurities of this kind generally consist of inorganic substances, and are chiefly confined to inorganic reagents. Although, under ordinary circumstances, there would be no probability of a reagent containing any of the organic poisons, such as strychnine, morphine, and the like, still an impurity of a reagent used for the detection of any of these poisons might lead to erroneous conclusions.

The analyst should never accept any reagent or chemical as pure until he has fully established its purity for himself; and if there be any possibility of its having become changed since last examined, the examination should be repeated. This latter precaution is necessary, since reagents, when frequently used for general analyses, are quite liable to become more or less contaminated; and some reagents may even speedily undergo spontaneous changes. All liquid reagents should be preserved in hard German-glass bottles, and handled only by means of perfectly clean pipettes. If poured from the mouth of the bottle, it is difficult to control the amount used; and, moreover, the portion left adhering to the neck of the bottle may by the action of the atmosphere become changed, and afterward fall back into the solution, and thus contaminate it. It need hardly be added that no other than pure *distilled* water should be used for the solution of reagents, and in all chemical operations.

In applying a reagent to a suspected solution, it should be borne in mind that the results may be much modified by the quantity employed. In some instances, a very slight excess of the reagent may entirely prevent the formation of a precipitate which would otherwise take place. Thus, a solution of morphine, when treated with a given quantity of potassium hydrate, may yield a copious crystalline deposit, while with slight excess of the reagent it may yield no precipitate whatever. On the other hand, a deficiency of reagent may produce results very different from those occasioned by other quantities. A limited quantity of sulphuretted hydrogen throws down from a solution of corrosive sublimate a *white* precipitate; while excess of the reagent produces a *black* deposit. Any quantity of a reagent above that necessary to produce the desired

result, is an excess, and may do harm, if only by diluting the mixture.

All *apparatus* employed in contact with the suspected substance under examination should either be of glass or of well-glazed porcelain, and be washed with scrupulous care. In fine, any article about to be thus employed, whose purity is not entirely above suspicion, should be rejected.

Qualifications of the analyst.—A chemico-legal investigation of this nature, as well remarked by Prof. Otto in regard to the detection of arsenic, should be intrusted only to an experienced chemist. He should not only be acquainted with the principles involved in the analysis, but know from experience how to perform it in all its details, and be able to defend his conclusions from any objections that might arise at a subsequent trial. If he be unacquainted with the details of the analysis of the special poison under consideration, he should first familiarize himself with them by repeated experiments upon known and minute quantities of the substance suspected to be present, under conditions similar to those under which it is supposed to exist. To point out the methods by which the presence of any of the poisons herein considered may be fully established, and to give directions whereby those having only a limited experience in this branch of chemistry may acquaint themselves with the details of the analysis, are among the objects of the following pages.

In the special consideration of the different poisons, they will be grouped together in accordance with their chemical relations or for convenience, rather than in regard to their physiological effects. They will be discussed under two general Parts of the work: Part First will contain the inorganic poisons, with which will be included Hydrocyanic and Oxalic acids; Part Second will be confined to the consideration of vegetable poisons.

As an Appendix will be added a chapter on the Nature, the various methods of Detection, and the Microscopic Discrimination of Blood.

PART FIRST.

INORGANIC POISONS.

INORGANIC POISONS.

CHAPTER I.

THE ALKALIES: POTASH, SODA, AMMONIA.

General Chemical Nature.—In their general chemical nature the alkalies, potash, soda, and ammonia, and their salts, form a quite natural and distinct group of compounds.* When in solution, either in their uncombined state or as normal carbonates, they have a strong alkaline reaction, immediately restoring the blue color of reddened litmus-paper. They differ from most other metallic oxides in being freely soluble in water; the same is also true in regard to many of their salts, especially their sulphides and carbonates. From their aqueous solutions they are not precipitated under any condition by either sulphuretted hydrogen, ammonium sulphide, or sodium carbonate; whereas all other metals are precipitated by one or more of these reagents. This difference of behavior is due to the fact that the sulphides and carbonates of the alkalies are freely soluble, whilst the corresponding salts of all other metals are insoluble in water. Nor do the alkalies precipitate each other when in solution in their free state; and the same is true, with very few exceptions, in regard to their salts. As potash and soda, and their salts, unlike ammonia and its salts, are not dissipated upon the application of heat, they are called *fixed* alkalies.

Physiological Effects.—Although the alkalies and many of their salts are highly poisonous, yet they have very rarely been administered criminally or taken for the purpose of suicide. They have,

* In the present consideration of the distinguishing properties of the above-named alkalies, the properties of the compounds of the very rare alkali-metals *lithium*, *cæsium*, and *rubidium* will be entirely excluded.

however, not unfrequently been taken by accident and produced fatal results. As the effects of the different alkalies upon the animal economy are very similar in their nature, they will in this respect be considered together; but treated of separately when considering their chemical properties.

Symptoms.—1. *Of the fixed Alkalies.*—When a strong solution of either of these compounds or of their carbonates is taken into the mouth, the individual *immediately* experiences a nauseous acrid taste, and there is rapid disorganization of the mucous membrane of the parts with which it comes in contact. On account of the immediate and exceedingly acrid taste of these substances, the solution is sometimes rejected from the mouth without any portion of it being swallowed. If the solution be swallowed, it gives rise to a sense of burning heat and constriction in the fauces, œsophagus, and stomach, followed by violent vomiting of mucous matters, which sometimes contain blood. These symptoms are generally followed by intense pain in the stomach, tenderness of the abdomen, bloody purging, great muscular prostration, and sometimes convulsions. The pulse becomes rapid, small, and thready; the skin covered with cold perspiration; and the mouth, tongue, and throat inflamed and swollen. If the patient survive a few days, there may be sloughing of the fauces, which may end in stricture of the œsophagus, and thus death finally take place from starvation. Death has in some instances resulted from inflammation and obstruction of the air-passages.

In a case reported by Dr. Ogle (*St. George's Hosp. Reports*, iii. 233), a woman swallowed a quantity of an impure solution of caustic potash. She vomited immediately, and soon after the mouth and fauces were found much corroded. Great pain was experienced in the region of the stomach and the course of the diaphragm. On the third day vomiting came on, and there was some dysphagia and pain at the top of the sternum, but no tenderness or pressure at the epigastrium. After several days the mouth and fauces were abraded, and later there was great tenderness and pain at the stomach; the pulse became quickened, the tongue shining and glazed. Subsequently nothing could be retained in the stomach, and the woman died, from inanition, something over two months after the caustic liquid had been taken. In another case related by the same writer, the taking of a similar solution was soon followed by bloody vomiting,

which continued three days; death ensued after some weeks, from exhaustion.

2. *Of Ammonia.*—The effects produced by strong solutions of ammonia, as common *aqua ammoniæ*, are much the same as those of the fixed alkalies and their carbonates; but in some instances it is even more severe in its action. With very few exceptions, instances of poisoning by this substance have been the result of accident; and in some of these death took place with great rapidity. In a case of poisoning by a solution of this kind taken with suicidal intent, quoted by Dr. Stillé, the symptoms were collapse, serous and bloody purging, bloody vomiting, excruciating pain in the abdomen, and death in six hours. If the patient survive the primary effects of this poison, he is less likely to die from secondary effects than in poisoning by the fixed alkalies.

In a case related by Dr. Stevenson (*Guy's Hosp. Reports*, xvii. 225), a man was admitted into the hospital who in the morning had drunk about a teaspoonful of strong liquor ammoniæ (sp. gr. .88). The lips, tongue, tonsils, and uvula were much swollen, red, and glazed, with here and there flakes of white epithelium resting upon the surface. There was some impediment to breathing. After complaining of slight pain in the abdomen, the patient turned over on his side, became blue in the face, and expired immediately, without any struggle for breath.

Dr. Garvin reports a case (*Boston Med. and Surg. Jour.*, Aug. 1880, 166) in which a man was given, by mistake, four tablespoonfuls of aqua ammoniæ, which he drank rapidly, not, however, quite draining the cup. He immediately rejected some of the liquid from the mouth, and soon afterward vomited, probably discharging a portion from the stomach. A terrible burning sensation of the mouth and fauces at once ensued; but not until two hours afterward did he complain of soreness any lower down, and at no time did that become a marked symptom. After about three-quarters of an hour some vinegar was administered, followed by demulcent drinks. These effects were followed by repeated vomiting of bloody matters, and death on the fifth day after the poison had been taken.

In another case a man swallowed with suicidal intent *eight ounces* of liquor ammoniæ. Four hours later, when admitted to the hospital, he was semi-conscious, the pupils were widely dilated, the breathing noisy and hurried, the pulse very rapid, and there was pro-

fuse sweating. He complained of great pain in the abdomen, vomited a quantity of blood, mucus, and shreds of mucous membrane. Six hours later, he was very hoarse and drowsy; his face dusky and skin dry. Next morning his lips were swollen, tongue dry, and the mucous membrane of the mouth partly eroded; the fauces were greatly congested, the mucous membrane œdematous, softened, and inflamed. There was great pain and tenderness in the abdomen on the slightest pressure. He had vomited blood twice since the night, and complained of burning pain in the throat and pit of the stomach, and there was incessant retching. He died thirty-six hours after swallowing the liquid. (*Medical Times*, Feb. 1879, 241.)

The *vapor of ammonia*, even when largely diluted with atmospheric air and inhaled, produces violent dyspnœa, severe pain in the throat, irritation and inflammation of the air-passages and lungs, and in some instances death. In the related case of a druggist, who accidentally inhaled the fumes of ammonia from a broken carboy, there was corrosion of the mucous membrane of the mouth and nostrils, great difficulty of breathing, feeble and irregular pulse, and a bloody discharge from the mouth and nose. These effects were followed by a most violent attack of bronchitis, during which the patient could not speak for several days; but he ultimately recovered. The injudicious use of this vapor for the purpose of rousing persons from a state of insensibility has in several instances been followed by fatal results.

The *carbonates of ammonium*, of which there are several, are less intense in their action than a solution of the free alkali, their intensity diminishing in proportion to the increase of carbonic acid present.

Period when fatal.—In poisoning by the caustic alkalies or their carbonates, death may take place within a short period from the immediate effects of the poison; or the patient may recover from the primary irritation and ultimately die from secondary results months or even years after the substance had been taken. In a case described by Mr. Dewar, a little boy who swallowed by mistake about three ounces of a strong solution of carbonate of potassium, died from its effects in *twelve hours* afterward. (*Edin. Med. and Surg. Jour.*, xxx. 309.) In another instance, related by Dr. Cox, a small quantity of deliquesced carbonate of potassium proved fatal in *twenty-four hours* to a child aged three years.

On the other hand, two sisters, aged respectively twelve and sixteen years, took by mistake about half an ounce of subcarbonate of potassium each. Violent symptoms immediately ensued, and in the case of the elder continued with little interruption for about *two months*, when death took place. In the case of the other, the symptoms abated after a few days; but they again returned, and finally proved fatal after the lapse of nearly three months. (*Beck's Med. Jur.*, ii. 524.) In a case reported by Dr. Deutsch, a solution estimated to contain about half an ounce of caustic potash did not prove fatal until after a period of twenty-eight weeks. And in another, a quantity of impure carbonate of sodium produced stricture of the gullet, of which the patient died two years and three months after having taken the poison. Sir C. Bell relates a case of this kind, in which death did not take place until after the lapse of twenty years.

Solutions of *ammonia* have proved rapidly fatal. In a case related by Plenck, a quantity of liquor ammoniæ poured into the mouth of a man who had been bitten by a mad dog caused death in *four minutes*. (*Christison on Poisons*, 194.) Dr. Kern relates the case of a man of intemperate habits, aged seventy years, who took two swallows of spirits of ammonia; he was immediately afterward seized with a sense of suffocation, cough, and vomiting, and, notwithstanding prompt treatment, he died within *four hours;* death being preceded by delirium, stupor, and spasms. (*Amer. Jour. Med. Sci.*, Jan. 1870, 275.) A case in which a solution of ammonia proved fatal in *six hours* has already been cited. In a case reported by Dr. Français (*Ann. d'Hyg.*, 1877, i. 556), ninety grammes (about three ounces) of aqua ammoniæ, taken by a young woman, did not prove fatal until the eighth day. The *vapor* of ammonia applied to the nostrils of a lad laboring under a fit of epilepsy induced bronchitis which proved fatal in forty-eight hours. In a somewhat similar case, death ensued on the third day.

Fatal quantity.—It is impossible at present to state with any degree of certainty the smallest quantity of either of the substances under consideration that might prove fatal. In most instances the effects will depend rather upon the degree of concentration under which the substance is taken, than upon the absolute quantity. In an instance recorded by Dr. Taylor (*op. cit.*, 328), one ounce and a half of the common solution of potash of the shops proved fatal to an adult in

seven weeks. The quantity of the caustic alkali taken in this case did not perhaps exceed *forty grains*, which is the smallest fatal dose we find recorded. There are not less than four cases reported, two of which have already been cited, in which *half an ounce* of the carbonate of potassium proved fatal: in all of these, as in the preceding case, death was due to the secondary effects of the poison.

Solutions of *ammonia* have proved fatal when taken in small quantity. In the case related by Dr. Stevenson, a *teaspoonful* of strong liquor ammoniæ proved rapidly fatal to an adult. And at least two fatal instances are reported in each of which not over *two drachms* of the solution had been taken.

Instances of recovery from solutions of this alkali have been of more frequent occurrence than from the fixed alkalies. A man swallowed by mistake three drachms of a strong solution of ammonia, and as much of the sesquicarbonate, dissolved in two ounces of oil; but under appropriate treatment he recovered in about eight days. (*Wharton and Stillé's Med. Jur.*, 502.) Dr. Blake reports a case in which a girl, aged fourteen years, swallowed a mixture of half an ounce of aqua ammoniæ and one ounce of olive oil, and, although she lingered in great agony for many weeks from the effects of the mixture, she eventually recovered. (*St. George's Hosp. Rep.*, 1870, 75.) In another case, a boy, aged two years, took half an ounce of very pungent spirits of hartshorn, and recovered. Instances are related in which recovery took place even after more than an ounce of the solution had been taken. In a case reported by Dr. Pellérin, a young woman with suicidal intent swallowed at a draught upwards of *ten drachms* of a solution of ammonia. Dr. Pellérin found the patient in the sitting position, having on her knees a basin containing a large quantity of stringy salivary fluid with a few streaks of blood. The face was pale, the eyes were haggard and injected. The lips presented much swelling, and also redness, which extended to the mouth and fauces. There was complete aphonia; pain in the pharynx and epigastrium; the pulse was slow, the limbs cold. The loss of voice lasted three days, and deglutition was almost impossible. Under active treatment the woman was convalescent in a week. (*Medico-Chir. Rev.*, April, 1857, 500.)

Treatment.—The antidote for poisoning by any of the free alkalies or their carbonates, is the speedy administration of a solution of some of the mild vegetable acids,—such as acetic acid in the form

of diluted vinegar, or the juice of any of the acid fruits,—by which the poison will to a certain extent be neutralized. Large quantities of olive oil have in some instances been administered with advantage. This substance may convert the alkali into a soap, and thus prevent its caustic action. Large draughts of milk may also be used with benefit. In poisoning by the vapor of ammonia, Dr. Pereira recommends the inhalation of the vapor of acetic or of dilute hydrochloric acid.

Post-mortem Appearances.—These will depend in a great measure upon the length of time the patient survived the taking of the poison. In acute cases, the mucous membrane of the parts with which the substance comes in contact is more or less disorganized, being inflamed and broken up in patches; sometimes there is extravasation of disorganized blood upon the walls of the organs thus affected, which causes them to present a bluish or black appearance. This appearance is sometimes well marked in the mouth. In some instances, large portions of the mucous membrane of the mouth, œsophagus, and stomach are entirely removed.

In Mr. Dewar's case, in which death was produced in twelve hours by a solution of carbonate of potassium, the appearances were much the same as those just described. Thus, the mucous membrane of the pharynx and œsophagus was almost entirely destroyed, and dark blood extravasated beneath the pulpy mass; in the stomach, the mucous membrane was destroyed in two places, and these patches covered with clotted blood. Similar appearances were found in the case that proved fatal in twenty-four hours.

In the case related by Dr. Ogle, in which a quantity of caustic potash proved fatal after about two months, the organs of the thorax, the tongue, fauces, and pharynx were found natural; but at the upper part of the œsophagus three distinct cicatrized bands were observed, contracting the mucous membrane; the lower part of the tube was much contracted, its lining membrane quite destroyed, and the muscular coat exposed. The external tissues of the œsophagus were much thickened, and the tube was strongly adherent to all the neighboring parts. The cardiac orifice of the stomach was so contracted as barely to admit the passage of a director; the mucous membrane at the pyloric end of the organ presented a large and dense cicatrix, which so involved the adjacent parts as to obstruct all communication with the duodenum, except by a small orifice which only admitted

an ordinary-sized probe. The other portions of the stomach, and the remainder of the intestinal tube, as also all the other abdominal organs, were healthy. In a case in which death was caused by the taking of a solution of caustic potash four months previously, there was found a stricture of the œsophagus four or five inches in extent, rendering swallowing impossible. (*Chem. News*, Oct. 1867, 197.) In Dr. Deutsch's case, already cited, the mucous membrane of the lower portion of the œsophagus was found so greatly thickened that the opening into the stomach was nearly obliterated.

In Dr. Kern's case, in which a solution of *ammonia* proved fatal in four hours, the mouth and throat were found denuded of epithelium, and inflamed; the stomach contained a bloody fluid having the odor of ammonia; at its lower portion the epithelium of the stomach was destroyed, and the muscular coat changed into a black pulpy substance. The duodenum and the serous coat of the stomach nearest the bowel were inflamed. The blood remained of a thin fluid consistence. In the case in which a teaspoonful of liquor ammoniæ proved rapidly fatal, related by Dr. Stevenson, the mucous membrane of the mouth and pharynx was found red and glazed. The œsophagus was intensely red throughout, more especially at its lower part, which was of a dark-purple color; this color ceased abruptly at the stomach. The upper portion of the œsophageal mucous membrane was shreddy in a longitudinal direction. The epiglottis was slightly œdematous; the loose tissue about the larynx much so. The mucous membrane of the trachea and bronchi was thickened and injected. Both lungs were gorged with blood and œdematous. A circular patch of the gastric mucous membrane, about four inches in diameter, was injected, and the membrane here was thin; elsewhere it was thick, pale, and coated with slimy mucus. Both sides of the heart contained dark fluid blood.

In the case in which eight ounces of liquor ammoniæ had been taken, there were signs of inflammation all along the digestive tract. The mucous membrane of the stomach was charred and destroyed, and there was great congestion as far as the lower end of the jejunum. The stomach contained about ten ounces of dark altered blood. In another case, fatal in three days, the lining membrane of the trachea and bronchi was softened and covered with layers of false membrane; while the larger bronchial tubes were completely obstructed by casts of this membrane. The mucous membrane of the gullet was soft-

ened, and the lower end of the tube completely destroyed. The anterior wall of the stomach contained an aperture about an inch and a half in diameter, through which the contents of the organ had escaped.

In *chronic* cases, the lower portion of the œsophagus and the stomach are frequently much contracted. The walls of the stomach are often thickened, and the lining membrane wholly destroyed. An ulcerated and gangrenous state of the mucous membrane of the stomach and intestines has also been observed. And in some instances other of the abdominal organs have been much disorganized.

NITRATE OF POTASSIUM.—This salt, commonly known by the name of *saltpetre* or *nitre*, has in several instances been taken by accident, with fatal results. To produce serious effects, however, it requires to be taken in large quantity, such as half an ounce or more. The symptoms usually observed are severe burning pain in the stomach and abdomen, nausea, vomiting and purging, followed by coldness of the extremities, tremors, and collapse. The effects of large doses have, however, been subject to considerable variation.

In a case recorded by Dr. Beck, a dose of this salt taken in mistake for Glauber's salt, proved fatal to an aged man in *half an hour;* and in an instance cited by Orfila, one ounce caused death in three hours. A man who took three ounces and a half of the salt at a dose, apparently suffered but little for five hours, when he suddenly fell out of his chair and expired. In a more recent case, about an ounce of the salt caused the death of a strong young man in six hours. When first seen by a physician, a few hours after taking the dose, the patient was lying on his back, completely insensible, the skin cold, clammy, and blue; pulse irregular, almost imperceptible; from time to time there were sudden contractions of the pectoral muscles, which continued for some seconds; the eyes were fixed, pupils greatly contracted and immovable. (*Jour. de Chim. Méd.*, Dec. 1873, 542.) Recovery has in several instances taken place even after so much as two ounces of the salt had been taken.

The *treatment* consists in the speedy removal of the poison from the stomach, and the subsequent exhibition of demulcents. No chemical antidote is known.

After death, the stomach has been found highly inflamed, mottled

with dark-colored patches, and the mucous membrane partially detached. Similar appearances have also been observed in the small intestines. In at least one instance, the coats of the stomach were perforated by a small opening.

In the case fatal in six hours, mentioned above, all the signs of asphyxia were found: thick black blood filled the right heart, and there was great congestion of the lungs. The bronchial ramifications were filled with froth; their mucous membrane was normal, as also that of the alimentary canal. The liver, spleen, and kidneys presented nothing abnormal; the brain was healthy, but the sinuses were gorged with thick black blood. Analyses of the blood and urine showed the presence of a potassium salt.

Chlorate of Potassium.—Although usually regarded as non-poisonous, this salt has of late years caused death in a number of instances. In one of these, an elderly man took in mistake for Epsom salt something over an ounce (thirty-five grammes) of potassium chlorate. Death, which followed in seven hours after the ingestion of the salt, was preceded by the following symptoms: vomiting, colic, and diarrhœa, general weakness and rigidity of the limbs. After death the skin of the dorsal and lumbar regions presented a slate-colored appearance. (*Med. Times*, Jan. 1881, 287.) In a case related by Dr. Kennedy (*Amer. Jour. Pharm.*, 1878, 112), about half an ounce of the salt proved fatal in seven hours, under vomiting, purging, and stupor, to a child aged two and a half years.

M. Marchand reports a series of cases in which four children, from three to seven years of age, took ten, twelve, and twenty-five grammes of this salt in less than a day, or at most thirty-six hours. They suddenly vomited; the urine was scanty and bloody, the skin yellow; there was rapid emaciation and loss of strength; finally cerebral symptoms, delirium, and coma, ending in death in three instances. In the *post-mortem* examinations of the fatal cases, and of animals used for experiment, the most characteristic lesions found were those of the blood and of the kidneys. The blood presented a peculiar brown or chocolate color, which was unchanged on exposure to the air. The kidneys were enlarged, of a brown color on the surface, and, under the microscope, the urinary canaliculi of the medullary substance were distended with brownish, granular cylinders, proceeding evidently from the disintegration of the red corpuscles; the renal

inflammatory action was of secondary importance. Under the spectroscope, the blood presented the spectrum of methæmoglobin.

The poisonous action of potassium chlorate, according to M. Marchand, is due to its oxidizing action upon the hæmoglobin of the blood, by which the corpuscles acquire a great tendency to agglutinate. Thus modified, the corpuscles accumulate in the different organs, but more especially in the kidneys, where they form brownish conglomerate masses. Death results either directly from the change in the blood, or from disturbance of the renal functions, whereby uræmic phenomena are produced. (*Annales d'Hygiène*, Nov. 1880, 485.)

Dr. Satlow, of Leipsic, reports the case of a boy, aged fifteen years, who swallowed a solution of potassium chlorate containing from twenty-five to thirty grammes of the salt. Soon after drinking the solution, the patient was seized with frequent vomiting of dark green masses very similar to thin fæcal discharges. Death ensued on the fourth day, resulting gradually from increased weakness of the heart, accompanied by dyspnœa and feelings of coldness and paralysis of the feet progressively extending upwards. On inspection, the blood was found of a peculiar brown color, the density of syrup, and the red corpuscles especially affected, being pale and glutinous, and gathered together in irregular clumps. A large quantity of reddish-brown fragments, supposed to be hæmoglobin, had been passed with the urine two days before death. (*Boston Med. and Surg. Jour.*, Jan. 1882, 81.)

In a case reported by Dr. Ferris, in which a large spoonful of the salt proved fatal to a strong man, on *post-mortem* examination the auricles of the heart were found distended to their utmost capacity by dark coagula, homogeneous, and of sufficient tenacity to support their own weight and sustain the coat of the cavities from which they were drawn. The large vessels communicating with the cavities were also full of similar coagula. On removal of the heart, but little blood flowed from any of the severed vessels. (*Medical Record*, 1873, 482.)

In a fatal case of poisoning by potassium chlorate, M. Ludwig examined the blood, the contents of the stomach, and the urine. The urine was turbid, acid in reaction, and contained an abundant sediment, composed of blood-globules in small number, and large granular casts. He failed to find the salt either in the blood, in the urine,

or in the contents of the stomach. (*Boston Med. and Surg. Jour.*, Feb. 1882, 127.)

Dr. T. Croft relates a case (*Gaillard's Med. Jour.*, July, 1883, 15) in which a young woman, directed to gargle with a solution of potassium chlorate, and occasionally swallow a little of the solution, used in this manner nearly half a pound of the salt within a few days. Violent symptoms then appeared, followed by death seven days later. At first there was violent vomiting and diarrhœa. This was soon followed by complete constipation and stoppage of the urinary secretion, persistent nausea, and general cyanosis, the blueness extending even to the finger-nails and toe-nails. After death, the skin became clear, and marble-like.

In a case reported by Dr. Bohn (*Med. Times*, May, 1884, 666), a man took in teaspoonful doses during thirty-six hours about two ounces of the salt. Symptoms of general collapse followed, and there was complete suppression of urine. A little urine drawn from the bladder contained blood-corpuscles and brownish tube-casts, and exhibited the spectrum of methæmoglobin. Death occurred on the third day, being preceded by jaundice. On inspection, the spleen, liver, and kidneys were found of a brown color, and the uriniferous tubules were filled with brownish masses.

The Tartrate, Sulphate, and Oxalate of Potassium have in several instances destroyed life. The noxious effects of the last-mentioned salt, however, chiefly depend upon the oxalic acid which it contains.

In a case of fatal poisoning by common *alum*, or *sulphate of potassium and aluminium*, in which a man, aged fifty-seven years, swallowed with some cold water, in mistake for Epsom salt, about an ounce of the calcined salt, the following symptoms were observed: at first a sense of violent constriction in the mouth, throat, and stomach; incessant nausea, followed by a single bloody vomiting, without any purging; extreme depression, great agony; small, quick pulse; rapid respiration, repeated syncope, and death in eight hours. The *post-mortem* examination revealed a yellow, abraded condition of the mouth, pharynx, and œsophagus, with swelling of the tongue and uvula; general inflammation of the peritoneum; kidneys much injected; bladder empty; heart dilated, with soft clots of a currant-jelly color. (*Annales d'Hygiène*, Jan. 1873, 192.)

Chemical Properties of the Alkalies.

Distinguishing properties.—Solutions of the *caustic* alkalies are distinguished from those of their carbonates by the latter effervescing, from the escape of carbonic acid gas, when acted upon by hydrochloric or any of the strong acids. Sulphate of Magnesium, at ordinary temperatures, throws down from solutions of the *normal carbonates* (*protocarbonates*) of the *fixed alkalies* a white precipitate; whereas with the *acid carbonates* (*bicarbonates*) it produces no precipitate. This reagent fails to precipitate solutions of either of the carbonates of ammonium.

Nitrate of Silver produces in solutions of the *fixed* caustic alkalies a brown precipitate, which is *insoluble* in excess of the alkali; while in a solution of *ammonia* it produces a somewhat similar precipitate, readily *soluble* in excess of the alkali: when, therefore, the reagent is not added in sufficient quantity, the ammoniacal solution fails to yield a precipitate. Solutions of the carbonates of either of the alkalies yield with this reagent a yellowish-white precipitate, which in the case of the fixed alkalies is *insoluble* in excess of the alkaline salt, while that from either of the carbonates of ammonium is *soluble* in excess of the alkaline compound. The precipitation of the acid carbonates by this reagent is attended with effervescence, due to the escape of carbonic acid gas, but this result is not observed in the case of the normal carbonates.

Corrosive Sublimate throws down from solutions of the fixed alkalies a bright *yellow* precipitate, which is insoluble in excess of the alkali; from the normal carbonates a reddish-brown; but in solutions of the acid carbonates it produces no precipitate. With ammonia and its carbonates this reagent produces a *white* precipitate, which is somewhat soluble in excess of the alkaline solution, especially in the presence of ammoniacal salts.

The different alkalies will now be separately considered, in regard to their chemical nature and reactions, and the methods by which they may be recovered from organic mixtures.

Section I.—Potassium Oxide.—Potash.

General Chemical Nature.—*Potassium oxide*, known also as *anhydrous potash*, is a compound of the elements potassium and oxygen, K_2O; in combination with the elements of water, with which it

unites with great energy, it forms *potassium hydrate*, KHO; thus, $K_2O + H_2O = 2KHO$. Potassium hydrate, known also as *hydrate of potash*, *potassa fusa*, and *caustic potash*, when pure, is a white, brittle solid; as usually met with in the shops in the form of little sticks, it has sometimes a grayish or brownish color, due to the presence of foreign matter. When exposed to the air, it deliquesces and slowly absorbs carbonic acid, becoming changed into the carbonate of potassium.

Potassium hydrate dissolves, with the evolution of heat, in about half its weight of water; it is about equally soluble in alcohol. Its solubility in alcohol enables us to separate it from many of its salts, such as the different carbonates, nitrate and sulphate, which are insoluble in this liquid. An aqueous solution of caustic potash changes an infusion of violets or of red cabbage to green, an infusion of turmeric to reddish-brown, and immediately restores the blue color of reddened litmus, even, according to Harting, when the alkali is dissolved in 75,000 parts by weight of water. A saturated aqueous solution of the pure caustic alkali has a density of about 2, and contains about 70 per cent. of the anhydrous alkali.

The following table, by Dalton, indicates approximately the percentage of anhydrous potassium oxide (K_2O) in solutions of the alkali of the different given specific gravities:

STRENGTH OF AQUEOUS SOLUTIONS OF POTASSIUM OXIDE.

Sp. Gr.	Percentage K_2O.	Sp. Gr.	Percentage K_2O.
1.78	56.8	1.36	29.4
1.68	51.2	1 33	26.3
1.60	46 7	1.28	23.4
1.52	42.9	1.23	19.5
1.47	39 6	1.19	16.2
1.44	36.8	1.15	13.0
1.42	34.4	1.11	9.5
1.39	32.4	1.06	4.7

Caustic potash, in its action upon animal tissues, is the most destructive of the alkalies. When rubbed between the fingers, by its chemical action on the skin, it imparts a soapy feel. It forms soluble compounds with many of the constituents of the animal tissues; and it may dissolve and perforate the coats of the stomach even more readily than the mineral acids.

The *salts* of potassium are colorless, except those in which the

constituent acid is colored; and they generally crystallize without water of crystallization, in which they differ in most instances from the corresponding salts of sodium. With very few exceptions, they are freely soluble in water.

SPECIAL CHEMICAL PROPERTIES.—Potassium compounds when heated upon a clean platinum wire, in the reducing blow-pipe flame, impart a *violet* color to the outer flame. This reaction may be entirely masked by the presence of even a small quantity of sodium, which gives a strong yellow color to the outer flame. In like manner, an alcoholic solution of the alkali or of any of its salts burns with a violet flame; but this reaction is also obscured by the presence of sodium compounds.

On account of the solubility of most of the compounds of potassium, there are but few reagents that precipitate it from solution, and these only when the solution is comparatively strong. Before applying any liquid test for the detection of potassium oxide or either of the alkalies, the absence of metallic oxides other than those of the alkalies should be established. This may be done by treating a small portion of the solution, acidulated with hydrochloric acid, with *sulphuretted hydrogen;* another, and neutral portion, with *sulphide of ammonium;* and a third portion, with *carbonate of sodium:* when, if these reagents fail to produce a precipitate, it follows that the metallic oxides mentioned are absent.

In applying a liquid reagent, a drop of the suspected solution may be placed in a watch-glass, and a small portion of the reagent added by means of a pipette. The mixture may then be examined by the microscope. If there be no immediate precipitate, it must not be concluded that the base in question is entirely absent; but the mixture should be allowed to stand, even in some instances for some hours, before deciding the entire absence of the substance.

In the following examinations of the behavior and limit of the different tests for the alkali under consideration, solutions of potassium chloride and of potassium nitrate were chiefly employed. The vulgar fractions used indicate the fractional part of a grain of anhydrous potassium oxide under the form of the salt employed, in solution in one grain measure of pure water; and the results, unless otherwise stated, refer to the behavior of *one grain* of the solution, treated in the manner above described.

1. *Chloride of Platinum.*

Platinic chloride throws down from solutions of salts of potassium, when not too dilute, a yellow precipitate of the double chloride of platinum and potassium, $2KCl; PtCl_4$, which, either immediately or after a very little time, becomes converted into beautiful octahedral crystals. Solutions of the free alkali should be treated with slight excess of hydrochloric acid, before the addition of the reagent. From dilute solutions, the presence of a little free hydrochloric acid, or of strong alcohol, facilitates the formation of the precipitate.

The precipitate is soluble in about one hundred and eight parts by weight of pure water at the ordinary temperature, but it is much more freely soluble in hot water; it is somewhat less soluble in water containing a trace of hydrochloric acid, and almost wholly insoluble in absolute alcohol. One part by weight of anhydrous potassium oxide or its equivalent in the form of a salt, yields 5.2 parts of the double salt.

1. $\frac{1}{50}$ grain of potassium oxide in the form of potassium chloride, in solution in one grain of water, yields with the reagent an immediate yellow crystalline precipitate, which very soon increases to a copious deposit. On stirring the mixture with a glass rod, it leaves lines of crystals where the rod has passed over the watch-glass.

   The same amount of potassium oxide in the form of nitrate, yields about the same results.

2. $\frac{1}{100}$ grain as chloride: crystals are immediately perceptible, and soon there is a fine crystalline deposit, which under the microscope presents the appearance represented in Plate I., fig. 1. When the potassium is in the form of nitrate, the precipitate is a little more slow in forming, and does not become quite so abundant.

3. $\frac{1}{250}$ grain: in about two minutes there is a perceptible precipitate, and after a little time a quite good crystalline deposit. If the mixture be stirred, it yields streaks of granules. From the nitrate of potassium, the precipitate is more slow to form and does not become so abundant, the crystals being confined to the border of the mixture. A 1–200th solution of the nitrate yields only about the same results as a 1–250th solution of the chloride.

4. $\frac{1}{500}$ grain: in about ten minutes crystals appear around the margin of the mixture; these increase, and in about three-quarters of an hour there is a quite satisfactory deposit scattered through the body of the drop. Stirring the mixture does not seem to facilitate the formation of the deposit. The forms of the crystals are much the same as illustrated above.

A 1–400th solution of the nitrate yields only about the same reaction as a 1–500th solution of the chloride. A 1–500th solution of the nitrate, however, will yield a perceptible deposit after standing about an hour. In these experiments, concentration of the mixture from evaporation was guarded against, perhaps, however, not perfectly.

Harting placed the limit of this test, when applied to a solution of the nitrate, at one part of potassium oxide in 205 parts of water. (*Gmelin's Handbook*, iii. 15.) Lassaigne fixed the limit for sulphate of potassium at one part of the alkali in 200 parts of water. (*Jour. Chim. Méd.*, 8, 527.) And for the acetate, Pettenkofer placed the limit at one part of potassium oxide in 500 parts of water, after standing from twelve to eighteen hours; but he states, when common salt is present, the reaction is limited to one part of the alkali in 100 parts of water, or even less. (*Gmelin*, x. 276.) Neither of these observers, however, states the quantity of solution employed in the experiment.

Fallacy.—Chloride of platinum also produces a similar yellow crystalline precipitate in solutions of salts of ammonium. The absence of these salts should, therefore, be established before concluding that the precipitate consists of the potassium compound. This may be done by adding some hydrate of lime or caustic potash to a small portion of the suspected solution and heating the mixture, when if it contain an ammoniacal salt the *odor* of this alkali will be evolved. Or, the precipitate produced by the platinum reagent may be heated to redness, when the potassium compound will leave a residue of chloride of potassium and metallic platinum, which, when treated with a small quantity of hot water and the filtered liquid acted upon by a solution of nitrate of silver, will yield a white precipitate of chloride of silver, due to the presence of the alkaline chloride; whereas the ammonium compound will leave upon ignition a residue of only metallic platinum, which, of course, will yield no precipitate with nitrate of silver.

2. *Tartaric Acid, and Sodium Tartrate.*

Tartaric acid, when added in *excess* to somewhat strong solutions of potassium compounds, produces a white crystalline precipitate of acid tartrate of potassium, $KHC_4H_4O_6$. From somewhat dilute solutions the precipitate is slow in appearing; in such cases, its formation is much facilitated by agitation, as also by the addition of alcohol. The precipitate is soluble in the mineral acids, and free alkalies and their carbonates; if, therefore, either of these substances be present in excess, the formation of the precipitate will be entirely prevented. The precipitate is insoluble in free tartaric and acetic acids.

When a solution of a potassium *salt* is treated with free tartaric acid, it is obvious that the acid of the salt is set free: thus, $KNO_3 + H_2C_4H_4O_6 = KHC_4H_4O_6 + HNO_3$. The acid thus set free may in a measure redissolve the potassium tartrate produced by the reagent, especially if it be one of the stronger acids. This elimination of the acid may be prevented by using the reagent in the form of a solution of the *acid tartrate of sodium* ($NaHC_4H_4O_6$), as first recommended by Mr. Plunkett. (*Chem. Gaz.*, xvi. 217.) Under these conditions, there would simply be an interchange of the metals, the sodium eliminated from the tartaric acid combining with the acid radicle set free from the potassium salt. This reagent is readily prepared by dividing a strong solution of tartaric acid into two equal parts, exactly neutralizing one of them with pure carbonate of sodium, and then adding the other.

In the following investigations a very strong solution of free tartaric acid, and a saturated solution of the acid tartrate of sodium, were employed as the reagents.

1. $\frac{1}{500}$ grain of potassium oxide in the form of chloride or nitrate, yields with *free tartaric acid* an immediate crystalline precipitate, which soon increases to a very good deposit. The *tartrate of sodium* produces much the same results, except, perhaps, the precipitate is somewhat more copious; the general forms of the crystals, however, are quite different. The neutral tartrate of sodium produces no precipitate.
2. $\frac{1}{1000}$ grain: crystals immediately begin to separate, and after a little time there is a good crystalline deposit. Plate I., fig. 2, represents the usual forms of the crystals produced by free tar-

taric acid. Acid tartrate of sodium produces a somewhat more abundant precipitate.

3. $\frac{1}{250}$ grain: in a few moments crystals appear, and very soon there is a quite satisfactory deposit. With the tartrate of sodium and chloride of potassium, the precipitate is somewhat more prompt in appearing. Plate I., fig. 3, represents the forms of crystals usually produced by the sodium reagent.
4. $\frac{1}{500}$ grain as chloride: within a few minutes granules appear; these soon become crystalline, and after a little time there is a quite satisfactory crystalline and granular deposit. From the nitrate of potassium the precipitate separates much more slowly, and is chiefly confined to the border of the mixture; under the microscope, however, the reaction is quite satisfactory. After standing about half an hour, either of these solutions yields a quite good deposit of crystals having the forms illustrated above. When acid tartrate of sodium is employed as the reagent, the precipitate is much more prompt in appearing, particularly from a solution of potassium chloride.
5. $\frac{1}{750}$ grain as chloride: after about ten minutes, small granules form along the margin of the mixture, and after some minutes more, there is a quite distinct granular and crystalline deposit. With the sodium reagent, granules and crystals appear within about four minutes, and there is soon a very satisfactory deposit.
6. $\frac{1}{1000}$ grain of the chloride, with acid tartrate of sodium: in about five minutes, crystals are just perceptible; and in about ten minutes, the deposit is quite distinct, but confined to the border of the drop. The crystals have the forms illustrated above, some of them being quite large.

From the above statements it is obvious that the chloride of potassium is the most favorable form of the alkali for the application of either of the above reagents. Pettenkofer placed the limit of the reaction of free tartaric acid, for solutions of the acetate of potassium, at one part of the anhydrous alkali in from 700 to 800 parts of water, after standing from twelve to eighteen hours.

Fallacy.—These reagents also produce similar crystalline precipitates from solutions of ammonia and its salts. The absence of this alkali may be established in the manner indicated under the preceding test.

3. *Picric Acid.*

A strong alcoholic solution of *Picric* or *Carbazotic* acid, when added in excess to solutions of caustic potash and of potassium salts, produces a yellow precipitate of picrate of potassium, $KC_6H_2(NO_2)_3O$, which is insoluble in excess of the precipitant and in alcohol. The precipitate contains the equivalent of 17.66 per cent. of anhydrous potassium oxide.

1. $\frac{1}{50}$ grain of potassium oxide in the form of chloride or nitrate, yields an immediate amorphous precipitate, which in a few moments becomes converted into a mass of long, regular, yellow crystalline needles, some of which extend entirely across the drop of liquid.
2. $\frac{1}{100}$ grain: crystals immediately begin to form, and in a very little time the drop becomes a mass of very long, slender, yellow needles, Plate I., fig. 4.
3. $\frac{1}{250}$ grain: in a few moments, crystals begin to form, and after a little time, a very good deposit of long needles.
4. $\frac{1}{500}$ grain: much the same results as in 3. From the nitrate of potassium the precipitate is not so prompt to form, nor is it as abundant as in the case of the chloride.
5. $\frac{1}{750}$ grain in the form of chloride, yields after a little time a perfectly satisfactory crystalline deposit.
6. $\frac{1}{1000}$ grain: after a few minutes, crystalline needles appear along the margin of the drop; after about fifteen minutes, the deposit becomes quite satisfactory, especially when examined by the microscope.

In applying this reagent it should be added in large excess. Thus, ten grains of a 1–500th solution of potassium oxide, when acted upon by a drop or two of the reagent, yield no precipitate, at least for some time; but if an *equal volume* of the reagent be added, it produces a precipitate within a few moments.

Fallacies.—Picric acid also throws down from solutions of ammonia and very strong solutions of caustic soda yellow crystalline precipitates. The microscope, however, will readily enable us to distinguish the potassium precipitate by its crystalline form from that of either of these substances. (Compare figs. 5 and 6, Plate I.) The reagent also produces yellow precipitates, some of which are crystal-

line, with many *organic* substances, especially the vegetable alkaloids. So, also, it occasions precipitates with certain other metals; but the absence of these, as already pointed out, should be established before applying the test.

In applying this test it must be remembered that a very strong alcoholic solution of the reagent, when added in certain proportion to *pure water*, may yield a yellow crystalline precipitate of free picric acid. The forms of these crystals, however, readily distinguish them from the potassium compound. In a 1–500th or stronger solution of the alkali, this distinction is very apparent to the naked eye; and in more dilute solutions, it is readily established by the microscope.

Other Reactions of Potassium Compounds.—L. de Koninck has recently shown that if a solution of a potassium compound be treated with excess of about a ten per cent. solution of Sodium Nitrite containing a little Cobaltous Chloride and Acetic Acid, the potassium is precipitated as the double *nitrite of potassium and cobalt*, the reaction being more sensitive than that of platinic chloride. (*Zeit. f. Anal. Chem.*, 1881, 390.)

We find that a drop of a 1–100th solution of potassium oxide in the form of a salt yields with a drop of this reagent an immediate, bright yellow, granular or crystalline precipitate. With a 1–500th solution the precipitate will appear in a very little time; and it may be obtained after a time from even a 1–1000th solution of the alkali. The precipitate is insoluble in hydrochloric acid, even when added in large excess; it is also insoluble in sulphuric and nitric acids.

This test is simply a modification of the well-known reaction for cobalt by potassium nitrite. The composition of the precipitate, according to Prof. Sadtler, is $6KNO_2$; $Co_2 6NO_2 + Aq$. The reagent produces a similar, but less sensitive, reaction with salts of ammonium. The reaction is not interfered with by the presence of salts of calcium, magnesium, iron, aluminium, or of zinc.

Hydrofluosilicic Acid in excess produces in strong solutions of potassium compounds a transparent gelatinous precipitate of the silicofluoride of potassium, which is insoluble in hydrochloric acid. In concentrated solutions this reaction is very satisfactory. A 1–50th solution of the alkali in the form of chloride yields, after a time, only a slight flocculent deposit.

Perchloric Acid produces in similar solutions a white crystal-

line precipitate of potassium perchlorate. So, also, a concentrated solution of SULPHATE OF ALUMINIUM, when added to concentrated solutions of the alkali previously acidulated with hydrochloric acid, precipitates crystals of the double sulphate of aluminium and potassium, or common alum: $K_2SO_4,Al_23SO_4+24H_2O$.

As a delicate reagent for the precipitation of potassium salts, M. Carnot recommends to dissolve one part (0.5 gramme) of SUBNITRATE OF BISMUTH in a few drops of hydrochloric acid; and, on the other hand, about two parts (1 gramme) of crystallized HYPOSULPHITE OF SODIUM in a few cubic centimetres of water. The second solution is added to the first, and then strong alcohol added in large excess. This mixture, or reagent, produces in solutions of potassium salts a yellow precipitate of the double *hyposulphite of bismuth and potassium*: $Bi_23S_2O_3$; $3KS_2O_3+2H_2O$. (*Chem. News*, Sept. 1876, 85, 120.) This reaction, it is said, is not interfered with by the presence of other bases.

SPECTRUM ANALYSIS.—This, as first applied by Professors Kirchoff and Bunsen, is by far the most delicate method yet discovered for the recognition of potassium,—as well as of sodium and many other volatile metals. It consists in introducing a small portion of the caustic alkali, or any of its salts containing a volatile acid, into the flame of a Bunsen gas-burner and allowing the rays of the colored flame to pass through a prism. The refracted rays are then examined by means of a small telescope, when, in the case of potassium, two distinct lines, one having a red color and the other indigo-blue, will be observed, which are characteristic of this metal. The authors of this method estimated that it would reveal the reaction of the 65,000th part of a grain of potassium, and the 195,000,000th part of a grain of sodium. (For the details of this method, see *Quart. Jour. Chem. Soc.*, Oct. 1860; also, *Fresenius's Qualitative Analysis*, London, 1877.)

Although spectrum analysis has very largely extended the scope of chemical research, enabling us in a few seconds to detect the presence of the most minute traces of many metals, and bringing to light substances of which heretofore we had no knowledge; yet, as it gives no indication whatever as to the *quantity* of the substance present, it is still doubtful whether it will be of any practical value in chemico-legal investigations, at least for the detection of the fixed alkalies,

since these are so universally distributed through the tissues and juices of both animal and vegetable structures.

Separation from Organic Mixtures.

When the suspected solution is highly colored or contains much organic matter, the tests for either of the alkalies cannot be satisfactorily applied directly to the mixture. If the solution has a soapy feel, a strong alkaline reaction, and is destitute of the odor of ammonia, even when a small portion of it is heated with hydrate of lime, the presence of one or other, or both, of the fixed alkalies, or of their carbonates, may be inferred.

Either of the fixed alkalies may be separated from their carbonates and organic matter, by evaporating the mixture on a water-bath to about dryness and digesting the cooled residue with absolute alcohol, which will dissolve the free alkali, while its carbonates, and other salts if present, will remain undissolved. The alcoholic solution is then concentrated to a small volume, and, if strongly alkaline and nearly colorless, at once neutralized with hydrochloric acid, and examined by the appropriate reagents. If, however, it contains much organic matter, before being tested it should be evaporated to dryness, the residue incinerated at not above a dull red heat until the organic matter is entirely destroyed, and the cooled mass dissolved in water; the aqueous solution is then examined in the ordinary manner.

Although the alkaline carbonates in their pure state are almost wholly insoluble in absolute alcohol, yet the presence of certain kinds of organic matter renders them slightly soluble in this menstruum. A small quantity of these salts may, therefore, be extracted along with the caustic alkali in the above operation. To ascertain the presence of fixed alkaline salts in the residue from which the free alkali was extracted by alcohol, the mass is incinerated in the manner directed above, and the cooled residue dissolved in distilled water.

Another method recommended for the recovery of the fixed alkalies and their carbonates from complex organic mixtures, is to evaporate the solution to dryness, incinerate the dry mass, and then separate the free alkali from its carbonate by means of absolute alcohol. This method has the advantage of at once destroying the organic matter, but the charring of this converts more or less of the free

alkali into carbonate, the quantity thus converted depending upon the relative amount of organic matter present. The amount of free alkali, therefore, furnished by this method would be somewhat less than originally existed; while by the preceding process the estimate of this substance might be somewhat too high.

Quantitative Analysis.—The quantity of caustic potash present in pure solutions of the free alkali or of its carbonates may be estimated by precipitating it in the form of the double chloride of platinum and potassium. For this purpose the alkali is converted into chloride, by the addition of hydrochloric acid, and the somewhat concentrated solution treated with slight excess of platinic chloride. When the precipitate has completely deposited, the mixture is concentrated on a water-bath to near dryness, and the cooled residue washed with strong alcohol, which will remove the excess of reagent added. The residue, consisting of the double salt, is then collected on a filter of known weight, washed with a little more alcohol, dried, and weighed. Every 100 parts by weight of the double salt thus obtained represent 22.96 parts of caustic potash, KHO; or 28.27 parts of anhydrous carbonate of potassium, K_2CO_3.

In all investigations of this kind, the original solution presented for examination should be carefully measured, and a given portion set apart for the quantitative analysis. From the amount of the alkali discovered in this the entire quantity present may, of course, be readily deduced.

Section II.—Soda.

General Chemical Nature.—This alkali, in the form of *sodium hydrate*, or *caustic soda*, NaHO, is a white, opaque, powerfully alkaline, caustic substance, which when exposed to the air absorbs water and carbonic acid, becoming converted into carbonate of sodium. In its chemical action upon the tissues it is somewhat less energetic than the potassium compound. It is readily soluble in water, with the evolution of heat, yielding a highly caustic liquid. The aqueous solution, according to Tuennermann, contains the following percentage of anhydrous sodium oxide, Na_2O, according to the different specific gravities of the solution:

STRENGTH OF AQUEOUS SOLUTIONS OF SODA.

Sp. Gr.	Percentage Na_2O.	Sp. Gr.	Percentage Na_2O.
1.428	30.22	1.194	12.69
1.375	26.59	1.163	10.87
1.327	22.96	1.123	8.46
1.298	20.55	1.094	6.64
1.277	18.73	1.067	4.83
1.257	16.92	1.033	2.41
1.228	14.50	1.016	1.20

The *salts* of sodium are colorless, unless containing a colored acid. They are readily soluble in water, and more disposed than the corresponding compounds of potassium to unite with water of crystallization. The crystallized normal carbonate (*protocarbonate*), as also several other salts, contains ten molecules of water of crystallization. Many of its salts speedily effloresce when exposed to the air.

Special Chemical Properties.—When caustic soda, or any of its salts, is heated in the inner blow-pipe flame, it communicates a strong *yellow* color to the outer flame, even when only a minute quantity of the alkali is present. The presence of potassium compounds, even in large quantity, does not obscure this reaction. The same coloration is developed when an alcoholic solution of the alkali is burned. By *spectrum analysis*, as already indicated, the reaction of the merest traces of sodium may be recognized.

On account of the free solubility of the compounds of sodium, there are but few reagents that precipitate it even from concentrated solutions. In fact,—besides the coloration of flame,—antimoniate of potassium and Polarized Light are about the only tests at present known whereby small quantities of this alkali can be recognized.

In the following investigations solutions of pure caustic soda were employed. The fractions refer to the fractional part of a grain of the anhydrous alkali, Na_2O, in solution in one grain of water; and the results, to the behavior of *one grain* of the solution.

1. *Metantimonate of Potassium.*

A solution of this reagent is prepared by supersaturating warm water with the pure salt and filtering the liquid when perfectly cold. The solution should always be freshly prepared when required for use.

Metantimonate of potassium throws down from somewhat con-

centrated solutions of caustic soda and of its neutral salts a white crystalline precipitate of sodium metantimonate, $NaSbO_3$. The forms of the crystals produced depend very much upon the strength of the solution. If the solution has an acid reaction, it should be carefully neutralized with potassium carbonate before the addition of the reagent, since otherwise free metantimonic acid or acid metantimonate of potassium may be precipitated. The reaction of the reagent is not prevented by the presence of moderate quantities of salts of potassium, except the carbonate, in which the sodium compound is more readily soluble than in pure water.

1. $\frac{1}{25}$ grain of sodium oxide, in one grain of water, yields with the reagent an immediate deposit of small granules and rectangular plates; at the same time irregular and tooth-shaped crystals, as represented in the upper left portion of Plate II., fig. 1, float upon the surface of the mixture.
2. $\frac{1}{50}$ grain yields an immediate crystalline precipitate, consisting principally of small elongated rectangular plates, as represented in the lower portion of Plate II., fig. 1.
3. $\frac{1}{100}$ grain: an immediate deposit, consisting chiefly of small octahedral crystals, as illustrated in the right-hand portion of fig. 1, Plate II.
4. $\frac{1}{250}$ grain: almost immediately very small granules appear, and soon there is a quite good crystalline deposit of small plates and octahedrons.
5. $\frac{1}{500}$ grain: after a little time, small crystals can be seen with the microscope; after several minutes, a very satisfactory deposit to the naked eye. If the mixture be stirred with a glass rod, it yields lines of granules along the path of the rod, and a more copious deposit.
6. $\frac{1}{1000}$ grain: on stirring the mixture, crystals become perceptible to the microscope in about five minutes; in about fifteen minutes, they become quite obvious to the naked eye; and after about half an hour, there is a perfectly satisfactory crystalline deposit.

Metantimonate of potassium fails to precipitate potassium compounds and ammonia, even from concentrated solutions; but it produces precipitates in solutions of many other metals: the absence of these, therefore, must be established before concluding that the precipitate consists of the sodium compound.

2. *Polarized Light.*

This test, which was first suggested by Prof. Andrews (*Chemical Gaz.*, x. 378), is founded upon the fact that platinic chloride, and also the double chloride of potassium and platinum, when placed in the dark field of the polariscope, have no depolarizing action, whereas the *double chloride of sodium and platinum* possesses this property in a remarkable degree.

To apply this test, its author recommended the following method. Having removed other bases by the ordinary methods and converted the alkalies into chlorides, a drop of the solution is placed on a glass slide and a very small quantity of a dilute solution of the chloride of platinum added, avoiding as far as possible an excess. This mixture is evaporated by a gentle heat till it begins to crystallize, then placed in the field of a microscope furnished with a good polarizing apparatus. On turning the analyzer till the field becomes perfectly dark, and carefully excluding the entrance of light laterally, the crystals remain invisible if only the potassium compound or the reagent alone be present, while the presence of the slightest trace of sodium is at once indicated by the beautiful display of color of its platinum double salt, $2NaCl\,;\,PtCl_4$. Prof. Andrews states that in this manner he obtained a distinct reaction from a quantity of chloride of sodium representing only about the 1–825,000th of a grain of the anhydrous alkali.

In applying this method, instead of evaporating the mixture by the application of heat, it is best to allow it to evaporate spontaneously, as it thus yields much larger crystals of the double sodium salt.

1. $\frac{1}{1000}$ grain of sodium oxide in the form of chloride, in one grain of water, when treated with a very small quantity of the reagent and allowed to evaporate spontaneously, leaves a good deposit of long, irregular crystals of the double salt, Plate II., fig. 3. This deposit, under the polariscope, furnishes a beautiful display of prismatic colors.
2. $\frac{1}{10,000}$ grain: quite a number of fine crystals, which in the field of the polariscope yield very satisfactory results.
3. $\frac{1}{100,000}$ grain: usually yields several quite distinct and satisfactory crystals. Sometimes the deposit is in the form of thread-like groups, which, when broken up by the point of a needle, form

small crystalline plates. In this manner, these thread-like masses may readily be distinguished from depolarizing shreds of dust, which are sometimes present.

4. $\frac{1}{500,000}$ grain: with the least possible quantity of reagent, yields a few small depolarizing crystalline plates. Even the 1–1,000,000th of a grain of the alkali will sometimes yield quite distinct results.

Before applying this test, the examiner should be certain that any potash present is entirely converted into chloride, otherwise he may be led into error.

Picric Acid.—It is usually stated by writers on this subject that this reagent produces no precipitate even in concentrated solutions of sodium hydrate, whereby this alkali is distinguished from potassium hydrate; but this is not the fact. Thus, one grain of a 1–25th solution of the former alkali yields with the reagent, within a little time, a quite copious crystalline deposit, Plate I., fig. 6; and a similar quantity of a 1–100th solution yields, after a time, a quite distinct crystalline reaction. Solutions but little stronger than the first mentioned become converted into a mass of crystals by the reagent.

The crystalline form of the sodium precipitate will usually serve to distinguish it from the potassium compound, as also from that produced in solutions of ammonia.

Tartaric Acid produces in *very concentrated* solutions of the alkali, especially if the mixture be stirred, a white crystalline precipitate of acid tartrate of sodium. In one grain of a 1–10th solution of the alkali the reagent produces, on stirring the mixture, after a few minutes, a mass of groups of bold crystals, Plate II., fig. 2. One grain of a 1–25th solution, under the same circumstances, yields, after ten or fifteen minutes, a quite satisfactory crystalline deposit. If this mixture be not stirred, it fails to yield a precipitate even after several hours. Solutions but little more dilute than this fail to yield a precipitate under any condition whatever, even after many hours.

Platinic Chloride fails to precipitate even the most concentrated solutions of sodium compounds.

As a micro-chemical test for sodium, A. Streng has recently advised (1883) to treat a drop of the solution with Uranium Acetate, when either immediately, or on spontaneous evaporation of the liquid, yellow tetrahedral crystals of *uranium sodium acetate* are formed.

These crystals contain only 6.6 per cent. of sodium, and are readily distinguished from the rhombic crystals of uranium acetate by their action on polarized light. (*Jour. Chem. Soc. Abstr.*, March, 1884, 366.) We have found this method serve for the detection of very minute quantities of sodium salts.

Separation from Organic Mixtures.—Caustic soda may be separated from organic mixtures in the same manner as already directed for the recovery of caustic potash (*ante*, 83).

Since, according to the researches of E. Donath, commercial caustic soda sometimes contains minute quantities of *arsenic*, even to the extent of 0.16 per cent. of arsenic acid, this contamination might sometimes give rise to embarrassment in poisoning by the caustic alkali. (*Jour. Chem. Soc. Abstr.*, 1881, 856.)

Section III.—Ammonia.

General Chemical Nature.—Ammonia, in its pure state, is a gaseous compound of Nitrogen and Hydrogen, NH_3, having a very pungent odor and powerfully alkaline reaction. The gas is readily absorbed by water, which is thereby increased in volume and diminished in density; at a temperature of 10° C. (50° F.), according to Davy, this fluid takes up about 670 times its volume of the gas, and then has a density of 0.875. A solution of this kind constitutes common *aqua ammoniæ*, and is usually regarded as a *hydrate of ammonium*, NH_4,HO. According to Sir H. Davy, the following table exhibits the percentage by weight of ammonia gas in pure aqueous solutions of different specific gravities:

STRENGTH OF AQUEOUS SOLUTIONS OF AMMONIA.

Sp. Gr.	Percentage NH_3.	Sp. Gr.	Percentage NH_3.
0.875	32.30	0.938	15.88
0.885	29.25	0.943	14.53
0.900	26.00	0.947	13.46
0.905	25.37	0.951	12.40
0.916	22.07	0.954	11.56
0.925	19.54	0.959	10.17
0.932	17.52	0.963	9.50

Aqua ammoniæ, when pure, is colorless, has a peculiar powerfully pungent odor, and a strong alkaline reaction, immediately restoring the blue color of reddened litmus-paper; on warming the blued paper, the red color reappears, from the dissipation of the alkali.

On heating a solution of ammonia, the gas is rapidly expelled with effervescence; when the liquid is evaporated to dryness it leaves no residue, unless foreign matter be present.

The *salts* of ammonia, usually named *ammonium salts*, are colorless, and readily volatilized upon the application of heat. With few exceptions, they are freely soluble in water. The fixed caustic alkalies readily decompose them, with the evolution of free ammonia.

Special Chemical Properties.—Solutions of free ammonia are readily recognized by their peculiar odor. The salts of this base, when heated on platinum foil, are completely dissipated, unless they contain a fixed acid or foreign matter, in which respect they differ from the salts of the fixed alkalies. When their solutions are treated with potassium or sodium hydrate, or with hydrate of lime, and the mixture gently warmed in a test-tube, the presence of the ammonia eliminated by the decomposition may be recognized by its odor; as also by its alkaline reaction upon moistened reddened litmus-paper; and also by the production of white fumes of ammonium chloride when a glass rod moistened with dilute hydrochloric acid is held over the mouth of the tube. By suspending a slip of moistened reddened litmus-paper *within* the tube and closing its mouth, the presence of very minute traces of the alkali may, at least after a time, be recognized.

The behavior of solutions of ammonia and of some of its salts, when treated with nitrate of silver and corrosive sublimate, has already been pointed out (*ante*, 73). When the alkali is added in excess to solutions of salts of copper, the liquid assumes a characteristic blue color.

In the following investigations of the reactions of ammonia, solutions of pure chloride of ammonium were employed. The fractions refer to the amount of gaseous ammonia present in *one grain* of the solution, which was the quantity employed for each reaction, unless otherwise stated.

1. *Platinic Chloride.*

This reagent produces in neutral and slightly acid solutions of ammonia a yellow octahedral crystalline precipitate of the double chloride of ammonium and platinum, $2NH_4Cl$; $PtCl_4$, which is but sparingly soluble in *diluted* mineral acids, and in the free alkalies. In appearance the precipitate closely resembles the corresponding

compound of potassium. A given quantity of ammonia in the form of chloride yields with the reagent a larger quantity of the double salt than the same quantity of caustic potash: one part by weight of the former yielding 13.1 parts, and one part of the latter only 5.2 parts, of the double compound.

1. $\frac{1}{50}$ grain of ammonia, in one grain of water, when treated with the reagent, the mixture immediately becomes converted into an almost solid mass of crystals. The precipitate is much more copious than that from a similar solution of a potassium compound, but the crystals are somewhat smaller, and a portion of the deposit is in the form of granules.
2. $\frac{1}{100}$ grain: in a very few moments a very copious crystalline deposit.
3. $\frac{1}{250}$ grain: the precipitate begins to appear within a few moments, and in a little time there is a quite good octahedral deposit, very similar to that from a 1–100th solution of potassium oxide (Plate I., fig. 1).
4. $\frac{1}{500}$ grain: crystals appear in less than half a minute, and in a little time they are quite copious.
5. $\frac{1}{750}$ grain: in about three minutes crystals are just perceptible; in about five minutes the deposit is quite satisfactory. The formation of the precipitate is somewhat hastened by stirring the mixture with a glass rod.
6. $\frac{1}{1000}$ grain: in about eight minutes crystals are perceptible to the microscope, and soon after they become quite obvious to the naked eye, especially along the margin of the mixture; after about half an hour there is a quite satisfactory deposit.

Solutions but little more dilute than the last mentioned fail to yield a precipitate even after many hours.

Fallacies.—The method of distinguishing the double chloride of ammonium and platinum from the corresponding potassium compound has already been pointed out under the special consideration of the latter (*ante*, 77). This reagent fails to produce a precipitate even in the most concentrated solutions of sodium salts.

2. *Tartaric Acid, and Tartrate of Sodium.*

These reagents produce in neutral solutions of ammonia, when not too dilute, a white crystalline precipitate of acid tartrate of ammonium, $NH_4,HC_4H_4O_6$, which in appearance is very similar to the

corresponding salt of potassium, but somewhat more soluble in water. It is soluble in the free alkalies and in dilute mineral acids.

1. $\frac{1}{50}$ grain of the alkali yields with *free tartaric acid* no immediate precipitate, but in a little time crystals begin to separate, and after a few minutes there is a very satisfactory deposit, the crystals having the same form as those from potassium oxide, Plate I., fig. 2. The *acid tartrate of sodium* produces much the same results, but the forms of the crystals are then similar to those illustrated in Plate I., fig. 3.
2. $\frac{1}{100}$ grain: after several minutes granules and small crystals appear, and after some minutes more there is a quite good crystalline deposit, chiefly confined, however, to the margin of the mixture. With tartrate of sodium, the precipitate is more prompt in appearing and becomes more abundant; the forms of the crystals are then the same as before by this form of the reagent.
3. $\frac{1}{250}$ grain: after ten or fifteen minutes some few granules form along the margin of the mixture; in about half an hour the deposit becomes quite satisfactory. The sodium reagent produces a more prompt and satisfactory reaction. The formation of the precipitate from this, as well as from the preceding solutions, is much facilitated by stirring the mixture.
4. $\frac{1}{500}$ grain yields with tartrate of sodium, after stirring the mixture some minutes, a distinct granular deposit, which, after a time, becomes quite satisfactory.

There is nothing in the physical appearance of the tartrate of ammonium to distinguish it from the corresponding precipitate produced from solutions of potassium.

3. *Picric Acid.*

An alcoholic solution of picric acid produces in neutral solutions of salts of ammonium a yellow crystalline precipitate of *ammonium picrate*, $NH_4,C_6H_2(NO_2)_3O$, which is insoluble in excess of the reagent.

1. $\frac{1}{50}$ grain of the alkali yields an immediate amorphous precipitate, which in a little time becomes a mass of yellow crystals. The form of the crystals is quite different from that of those produced by the reagent from solutions of either of the fixed alkalies.

2. $\frac{1}{100}$ grain: almost immediately crystals begin to separate, and in a little time there is a quite good deposit. Under the microscope, the crystals present the appearances illustrated in Plate I., fig. 5, which readily distinguish them from the corresponding salts of potassium and sodium.
3. $\frac{1}{250}$ grain: in a few moments small rough needles begin to form, and very soon there is a good crystalline precipitate, in form quite unlike that from potassium compounds.
4. $\frac{1}{500}$ grain: in a few minutes needles begin to separate along the margin of the drop, and after a little time there is a satisfactory deposit.
5. $\frac{1}{750}$ grain: after some minutes, small needles appear; after some minutes more, there is a quite satisfactory deposit of needles, plates and cubes, which might readily be confounded with the deposit from dilute solutions of potassium compounds.

4. *Nessler's Test.*

When a solution of iodide of potassium and mercuric iodide in the presence of potassium hydrate is acted upon by ammonia, the latter is decomposed with the formation of an insoluble compound, known as *dimercur-ammonium iodide*, NHg_2I,H_2O.

The test-fluid is prepared by dissolving 20 parts by weight of pure potassium iodide in 50 parts of pure water, and adding mercuric iodide to the solution until it is no longer dissolved, which will require about 30 parts of the mercuric salt. The liquid will now contain the double iodide of potassium and mercury, $2KI; HgI_2$. The solution is diluted with three volumes of water, and the mixture allowed to stand some hours, when any excess of the mercuric iodide will separate in the crystalline form. The fluid is then filtered, and two measures of the filtrate mixed with three measures of a strong solution of potassium hydrate; this mixture is employed as the reagent. Should the liquid become turbid upon the addition of the potash solution, it is again filtered.

In the absence of mercuric iodide, the reagent mixture may be prepared by treating a solution of potassium iodide with a saturated solution of mercuric chloride, until a slight permanent precipitate is formed; a strong solution of potassium hydrate is then added, and the mixture allowed to stand until the liquid becomes clear, when it is decanted.

1. $\frac{1}{100}$ grain of ammonia as chloride, in one grain of water, yields, with a drop of the reagent, a very copious, beautiful orange-colored amorphous precipitate, most of which dissolves, with the production of a colorless solution, in excess of free ammonia, and of chloride of ammonium, leaving a slight, cream-colored residue. The precipitate is readily soluble, to a colorless solution, in hydrochloric acid.
2. $\frac{1}{1000}$ grain yields a quite copious precipitate, having a fine orange color.
3. $\frac{1}{10,000}$ grain: a very good, reddish-yellow deposit. Five fluid-grains of the solution yield a fine orange precipitate.
4. $\frac{1}{50,000}$ grain: an immediate yellow turbidity, which very soon assumes an orange tint, followed by a good flocculent precipitate, having a light-yellow color. Ten fluid-grains of the solution, with a drop of the reagent, yield an almost immediate, orange-colored muddiness, which slowly subsides to a deposit of the same color.
5. $\frac{1}{100,000}$ grain: an immediate cloudiness, and in a very little time the mixture contains suspended flakes, which have a dirty-white color. Five fluid-grains of the solution yield a bright-yellow turbidity, and soon the mixture acquires a slight orange tint.
6. $\frac{1}{500,000}$ grain: after a little time, a just perceptible cloudiness. Five fluid-grains of the solution very soon assume a pale-yellow color, which on heating the mixture is changed to a very slight orange hue.
7. $\frac{1}{1,000,000}$ solution: five fluid-grains of the solution, after a little time, assume a very pale-yellow color, which on the application of heat is changed into the slightest perceptible tint of orange. The color of this, and of other dilute solutions, is best seen by transmitted light.

The extreme sensibility of this test is explained by the circumstance that 17 parts by weight of ammonia yield 559 parts of the mercury compound, in accordance with the following reaction:

$$NH_3 + 2(2KI;\ HgI_2) + 3KHO = NHg_2I,H_2O + 7KI + 2H_2O.$$

According to J. Nessler, the presence of alkaline chlorides and oxysalts has no injurious influence upon the reaction of this reagent; and iodide of potassium is injurious only when sufficient caustic potash has not been added. But the reaction is not produced in the presence of potassium cyanide and potassium sulphide, even in con-

centrated solutions of ammonia and the presence of great excess of potassium hydrate.

MERCURIC CHLORIDE ($HgCl_2$) produces in solutions of *ammonium hydrate*, even when highly diluted, a white precipitate of *mercur-ammonium chloride*, NH_2HgCl; thus: $2NH_3 + HgCl_2 = NH_2HgCl + NH_4Cl$. When the ammonia is present in the form of a salt, a little sodium carbonate solution should be previously added to the mercuric reagent, both solutions being quite dilute. This mixture separates from solutions of free ammonia and its salts the precipitate before mentioned in combination with mercuric oxide, NH_2HgCl,HgO. The reaction will now manifest itself even in solutions containing only the minutest trace of the alkali. This reaction was first observed by M. Bohlig.

PHOSPHO-MOLYBDATE OF SODIUM, according to Sonnenschein (*Chem. Gaz.*, x. 411), will readily detect the presence of one part of chloride of ammonium in 10,000 parts of water. The reagent is prepared by igniting the yellow precipitate produced by adding molybdate of ammonium to an acidulated solution of sodium phosphate to expel the ammonia; any molybdic acid reduced in this operation is reoxidized by nitric acid, the excess of which is expelled by heat. The residue is then dissolved in sodium carbonate, the solution supersaturated with hydrochloric acid, and the mixture heated, after which any precipitate that has formed is redissolved by the addition of more acid.

This liquid, when employed as a reagent, produces in solutions of salts of ammonia a yellow precipitate of phospho-molybdate of ammonium which, according to Sonnenschein, contains only 4.411 per cent. of gaseous ammonia. The reagent produces a similar yellow precipitate in tolerably concentrated solutions of salts of potassium; but it fails to precipitate solutions of sodium salts.

Metantimonate of Potassium produces no precipitate, even in concentrated solutions of salts of ammonia or of the free alkali.

SEPARATION FROM ORGANIC MIXTURES.

Unless the ammonia be present only in extremely small quantity or combined with an acid, the liquid will have an alkaline reaction

and give out the odor of the alkali. Ammonia and its carbonate may be separated from organic solutions by *distilling* the liquid, at a moderate heat, in a retort the beak of which is provided with a perforated cork carrying a small tube, which is bent at an obtuse angle and made to dip beneath the surface of a very small quantity of pure water, contained in a well-cooled receiver. Any of the alkali or its carbonate present will be vaporized by the heat and pass along with the vapor of water into the receiver; the solution thus obtained may be tested in the ordinary manner.

If after distilling over about one-eighth of the contents of the retort no ammonia yet appears in the distillate, it may be concluded that none of the free alkali or its volatile salt is present. It may, however, be present in the form of some of its more fixed salts. To ascertain this, the contents of the retort are treated with strong alcohol, which will, in part at least, coagulate the organic matter; the mixture is then filtered, the filtrate treated with potassium hydrate or hydrate of lime, and distilled as before. Any ammoniacal salt present will now be decomposed by the alkali added, with the evolution of free ammonia, which will appear in the distillate. In some instances it is best to replace the pure water placed in the receiver by a very dilute solution of hydrochloric acid, whereby the ammonia will be more effectually absorbed, in the form of chloride of ammonium.

If the mixture under examination contains organic matter in a state of decomposition, this may give rise to ammonia. In mixtures of this kind it may be difficult or even impossible to decide the true source of the ammonia. If it be the contents of the stomach that are thus examined, the quantity of the alkali recovered and the *post-mortem* appearances may readily decide its origin.

Quantitative Analysis.—This may be effected by precipitating the alkali in the form of double chloride of ammonium and platinum, and treating the precipitate in the same manner as directed for the estimation of potassium compounds (*ante*, 84). The double ammonium salt contains 7.62 per cent. by weight of pure ammonia (NH_3).

Every 17 grains of real ammonia correspond to 52.6 grains of the most concentrated *aqua ammoniæ*, which measure a few drops over one fluid-drachm. Or, three parts by weight of a concentrated aqueous solution of the gas contain about one part by weight of free ammonia.

CHAPTER II.

THE MINERAL ACIDS: SULPHURIC, NITRIC, AND HYDROCHLORIC.

General Nature and Effects.—The above-named mineral acids form a group of compounds the members of which are quite similar, both in respect to their general chemical properties and their effects upon the animal system. They possess the property of acidity in the most eminent degree, such as reddening blue litmus, perfectly neutralizing free alkalies, and decomposing the salts of other acids. They are more or less decomposed when brought in contact with many of the metals, such as zinc, iron, copper, and mercury, with the formation of their respective salts. Sometimes this decomposition takes place at ordinary temperatures, but at other times only upon the application of heat. Most of the salts of these acids are readily soluble in water.

In their powers to corrode and destroy organic substances the mineral acids stand pre-eminent. When brought, in their somewhat concentrated state, in contact with living animal tissues, they rapidly destroy their organization and vitality; in this manner they may speedily occasion death by their direct chemical action. Due to this action, they also speedily affect or entirely destroy various articles of clothing with which they come in contact: this property is sometimes of considerable importance in a medico-legal point of view.

Numerous instances are recorded in which these substances occasioned death; but, with few exceptions, the poison was taken either with suicidal intent or as the result of accident. In fact, from their immediate and powerfully corrosive action on the mouth, there is perhaps no poison which, for criminal purposes, could not be resorted to with greater safety from detection than either of these acids; yet cases are not wanting in which they were thus employed.

Section I.—Sulphuric Acid.

This acid has long been known under the name of *oil of vitriol*, which name it received from the fact that it was prepared from *green vitriol*, or ferrous sulphate. As met with in the shops, it is a dense, powerfully acrid and corrosive, oily liquid, with frequently a more or less brownish color. When brought in contact with organic substances, it speedily chars them. In proportion as it is diluted with water, it loses its oily appearance and power of acting upon organic tissues. As a poison, it has been principally used in the form of the commercial acid, yet instances of poisoning by *sulphate of indigo*, which is a solution of indigo in the concentrated acid, and by *aromatic sulphuric acid* of the Pharmacopœias, have also occurred.

Instances of poisoning by this acid have been of much more frequent occurrence than by either of the other mineral acids. But, as already intimated, it has rarely been administered criminally. Of twelve cases of poisoning by this substance collected by Dr. Cozzi, in a hospital in Florence, eleven were the result of suicide. Dr. Christison has collected several instances in which children were murdered by the acid being poured down the throat. A case is also reported in which a man was murdered in a similar manner while he lay asleep; and another, in which it was thus administered to a woman while she was intoxicated. A singular practice of secretly throwing the acid upon persons for the purpose of disfiguring them or of destroying their dress has been of not unfrequent occurrence, both in this country and in Europe.

Symptoms.—The direct effects of sulphuric acid will, of course, depend much upon the degree of its concentration, and the quantity taken. When taken in its concentrated state, all the soft parts of the mouth and throat are immediately more or less corroded and destroyed, and assume a white appearance; and if the poison has been swallowed, the lining membrane of the œsophagus and stomach will be acted upon in the same manner. These effects will be followed with intense burning pain in the mouth, throat, and stomach, alteration of voice, gaseous eructations, and violent vomiting. The vomited matters have usually a brownish or black color, strongly acid properties, and contain disorganized membrane and blood. As the case advances, there will be excruciating pain in the

bowels, impaired respiration, difficulty of swallowing, coldness of the extremities, and great prostration. The pulse becomes weak and irregular, the countenance ghastly, and the body covered with cold perspiration. The bowels are usually much constipated, and the urine scanty. The inside of the mouth and throat frequently becomes covered with sloughs. The mental faculties usually remain unimpaired.

Such are the symptoms usually observed in poisoning by this acid in its concentrated state; but it is obvious that they may not all be present in a given case. The vomiting, which in most instances is either immediate or within a very short period, has been delayed for half an hour or longer. The action of the acid may be confined to the mouth, the poison having been thrown out without any portion of it being swallowed. In such cases, however, it may produce death by asphyxia, from the closure of the air-passages. On the other hand, the mouth may escape the local action of the acid, it having been administered in a spoon passed back into the throat, as in a case cited by Dr. Taylor. If the acid has come in contact with the lips or other parts of the external skin, they at first present a white appearance, which afterward becomes yellowish-brown.

In a case reported by Mr. Corfe, a man swallowed about *half a pint* of the acid, but a large portion of it was immediately rejected. The patient suffered intense agony, and soon after the extremities were cold and mottled, the pulse small and feeble; the epithelium on the tongue and lips was partially removed, and that on the fauces more extensively detached. Death took place twenty hours after the acid had been swallowed. In another case, a woman, aged fifty years, took about *half an ounce* of the acid. The moment it reached her throat, she seemed to be strangled, and fell. In about an hour afterward, vomiting having occurred several times, she complained of burning pain in the region of the stomach, but after an hour or two the pain entirely disappeared. The pulse was small and intermitting; the mouth presented the appearance of having been smeared with milk, and the epiglottis was much enlarged, but the voice was almost natural. The patient gradually sank, and died about forty hours after taking the acid, the mind remaining clear until death.

When swallowed in its *diluted* state, sulphuric acid produces much the same symptoms as those just described, only that they are less prompt in appearing, and the local action of the poison is less

violent. The extent of this difference will, of course, depend upon the degree of dilution of the acid.

Period when Fatal.—In fatal poisoning by this acid, death usually takes place in from twelve to thirty-six hours; but this event has occurred within an hour, and again it has been delayed for weeks, and even months. Dr. Christison cites a case in which a child, while attempting to swallow strong sulphuric acid by mistake for water, *died almost immediately*, to all appearances from suffocation caused by contraction of the glottis; it was ascertained after death that none of the poison had reached the stomach. (*Op. cit.*, 132.) Mr. Traill reports the case of a washerwoman, who took by mistake a wineglassful of the commercial acid, having a specific gravity of 1.833, and, although actively treated, died in *one hour* afterward. After death, a perforation was found in the stomach, and the peritoneum was greatly inflamed from the escape of the acid from the stomach. An instance is also related by Prof. Casper, in which the poison, administered by an unnatural mother to her own child, aged one year and a half, caused death, in spite of the antidotes administered, in *one hour*. (*Forensic Medicine*, ii. 75.) These are the most rapidly fatal cases yet recorded. Not less than three cases, however, are reported in which death occurred in *two hours;* and several in which death took place in from three to five hours. In three other cases, death took place in four and eleven days respectively in adults, and in the case of a child seventeen months old, in seven hours.

In poisoning by sulphuric acid, as in the case of the caustic alkalies, the patient may recover from the immediate effects of the poison, and yet die from secondary causes long afterward. In such cases, nervous symptoms and general derangement of the assimilating organs usually manifest themselves, and death is the result either of chronic inflammation of the stomach and bowels, or of stricture of some part of the alimentary tube. Several instances are reported in which death did not take place until from the *fifteenth* to the *twentieth* day after the poison had been taken; and Dr. Beck quotes a case not fatal until after the lapse of *two months*. In an instance reported by Dr. Wilson, life was prolonged for over *ten months*. During the progress of this case, the thickened lining membrane of the œsophagus came away in the form of a firm cylindrical tube, eight or nine inches in length. The most protracted case in this respect yet recorded is that quoted by Dr. Beck (*Med. Jur.*, ii. 472), in which

the patient survived the taking of the poison *two years*, when death supervened from the effects of stricture of the œsophagus.

Fatal Quantity.—The effects of given quantities of sulphuric acid have by no means been uniform. They will be influenced much by the condition of the stomach, as to the presence of food, and the degree of concentration of the acid, as also, of course, by the promptness with which remedies are employed. In many instances it is difficult to determine exactly how much of the poison has been retained in the body, even when the quantity originally taken is accurately known, since much of it is often rejected from the mouth as soon as taken.

The smallest fatal dose yet recorded is in a case quoted by Dr. Christison, in which half a teaspoonful, or about *thirty minims*, of the concentrated acid caused the death of a child, one year old, in twenty-four hours. The same writer quotes another instance, in which *one drachm*, taken by a stout young man, proved fatal in seven days. (*Op. cit.*, 131.) In a case already mentioned, about *one drachm and a half* of the acid, poured into the mouth of a man while asleep, caused death in forty-seven hours.

On the other hand, recovery has not unfrequently taken place after large doses of the acid had been swallowed. Thus, not less than two instances of this kind are related, in each of which *two ounces* of the concentrated acid had been taken. And Dr. Beck quotes a case in which a man recovered after having swallowed *four ounces* (whether by weight or by measure not stated). This is the largest dose that we find recorded from which there was recovery.

Treatment.—There are many substances that will perfectly neutralize this acid, yet on account of its very rapid local action, at least in its concentrated state, it is not often that chemical antidotes can be administered sufficiently early to prevent serious injury. Common chalk and calcined magnesia, suspended in milk, have generally been recommended, and will answer the purpose very well. The alkaline carbonates, properly diluted with water or milk, have also been strongly advised, and are perhaps preferable. In the administration of the alkaline carbonates, it must be remembered that they themselves, in large quantities, are highly poisonous. Oily emulsions, soapsuds, and milk alone may be employed with advantage.

Several instances are related in which the timely administration

of one or other of these antidotes saved the life of the patient, even after very large quantities of the poison had been taken. The exhibition of the antidote should always be followed by large draughts of tepid water or demulcent fluids, to promote vomiting. The whole of the acid, however, may be neutralized and removed from the stomach, and yet death take place from the effects of its primary action. On account of this local action, the patient is sometimes unable to swallow when first seen by the physician. Under these circumstances the poison may be withdrawn by means of the stomach-pump; but, for obvious reasons, this instrument should be used with great caution, and employed only as a final resort.

Post-mortem Appearances.—In poisoning by sulphuric acid, the pathological appearances are more frequently peculiar and characteristic than, perhaps, in the action of any other poison. These appearances, however, will be much modified by the degree of concentration of the acid, and the length of time the patient survived after it had been taken. In the taking of the poison it not unfrequently happens that drops of it become sprinkled over the face, neck, and other portions of the skin; in such cases, if not very protracted, these parts will present dark-brown spots or stains. In the case cited above from Casper, in which death took place in an hour, dirty-yellow parchment-like streaks, arising from the trickling down of the acid, extended from the angle of the mouth to the ear; similar stains were present on the arms and hands of the child. The tongue was white and leathery, and had no acid reaction. The stomach, both externally and internally, was quite gray, and filled with dark, bloody, acid mucus; its tissues fell to pieces when touched; the vena cava was moderately filled with a cherry-red syrupy and acid blood; and the liver and spleen were congested with blood of the same character; the heart contained only a few drops of blood. The tissues of the œsophagus were quite firm, and its mucous membrane had a grayish color, and an acid reaction; the larynx and trachea were normal.

In recent cases, the mucous membrane of the tongue and of the mouth is generally more or less corroded, and of a white, but sometimes of a deep-brown color; in some instances large patches of this membrane are entirely destroyed. Similar appearances are usually found in the fauces, and throughout the length of the œsophagus. The lining membrane of this organ is sometimes much thickened

and partially detached. Instances are recorded, however, in which the mouth and œsophagus presented but few signs of the local action of the poison.

The stomach generally presents a brownish or black appearance, due to the carbonizing action of the acid; its blood-vessels are frequently much engorged with dark coagulated blood, and its tissues so soft as to be readily lacerated, even by the slightest pressure. Sometimes this disorganization is confined to patches, whilst in others it extends in the form of lines or streaks; often the pylorus presents the most decided marks of disorganization. The contents of the stomach are usually thick and have a brownish or charred appearance and a highly acid reaction. If the stomach become perforated, as not unfrequently happens, the acid may escape and exert its chemical action upon the surrounding organs; but this organ may become perforated and its contents not escape. The aperture of the perforation usually presents a roundish appearance, and has thin, black, irregular edges. Sometimes there are several such perforations. In one instance, the perforation measured about three inches in diameter, and was bordered by thickened edges of a dark-brown, cinder-like appearance. A few instances have occurred in which there were no marks of the chemical action of the poison, except in the neighborhood of the perforation.

The duodenum and other portions of the small intestines have in some instances presented signs of corrosion similar to those observed in the stomach. Instances are reported, however, in which there was little or no abnormal change in these organs, even when the stomach was extensively disorganized.

In making these examinations, the inspector should not forget that the action of the acid may be confined to the mouth and throat, none of the poison having passed into the stomach. In such cases, as also in others, the air-passages may be much corroded and inflamed. So, also, it should be remembered that when the acid is swallowed in its diluted state, or the stomach contains much food or liquid, this organ may present simply signs of inflammation, instead of the disorganized appearances described above; even when, however, the acid is much diluted, the inside of the stomach may present a blackened appearance.

In the case related by Mr. Corfe, the epithelium was found detached or corrugated from the base of the tongue to the cardiac

extremity of the stomach. The interior of the stomach, and, for six inches below the pylorus, all the tissues, presented the appearance of being covered with a layer of black pitch, due to the charred state of the tissues. The ileum was also corroded. The blood in the left auricle of the heart was black and clotted; the left ventricle was empty, and rigidly contracted. In the case in which about half an ounce of the acid proved fatal to a woman in about forty hours, the mucous membrane of the cheeks, gums, and tongue was not destroyed, but the epiglottis was covered by a thick layer of false membrane. The lining membrane of the œsophagus was of a dirty-ash color, and could readily be removed. The cardiac orifice of the stomach did not show any marks of the action of the acid, but the large curvature at its cardiac extremity presented several strong ridge-like elevations; at the pyloric extremity of the organ the action of the acid was less intense. The cavities of the heart were empty, except the right ventricle, which contained about half an ounce of dark coagulated blood.

In a number of cases of acute sulphuric acid poisoning examined by Prof. Casper, the *blood* had in every instance a cherry-red color, a more or less ropy consistency, and an acid reaction. He also relates an instance of similar poisoning, in which he found the pericardial and amniotic fluids of a decidedly acid reaction, the person poisoned being pregnant. (*Forensic Medicine*, ii. 58, 83.) In the case of another pregnant woman, quoted by Dr. Beck (*Med. Jur.*, ii. 475), the amniotic fluid, as well as that found in the pleura, peritoneum, heart, and bladder of the fœtus, had an acid reaction. It need hardly be remarked that this acid condition of the fluids of the body would be found only in recent cases.

According to Casper, the bodies of persons poisoned by this acid, and perhaps by the other mineral acids, remain fresh and without odor for an unusual length of time. He attributes this condition to the free acid neutralizing the ammonia evolved during the first stages of the process of putrefaction.

When the patient survives the primary effects of the poison and dies from secondary results, the appearances will, of course, differ from those described above. In such cases the body is usually extremely emaciated, and one or more portions of the alimentary canal are much contracted. In Dr. Wilson's case, in which life was protracted for over ten months, the upper third of the œsophagus shone

like an old cicatrix, and the lower two-thirds were thickened, narrowed, and very vascular; the stomach contained a perforation, which was surrounded with softened edges.

In a case in which a woman swallowed a quantity of strong sulphuric acid, but did not die from its effects until about six weeks afterward, on inspection the mouth and fauces were found quite recovered from the effects of the acid, but there was complete absence of the mucous membrane of the œsophagus. The mucous membrane of the stomach was quite black and partially detached at the cardiac extremity, and underneath it were patches of fibrinous exudation a quarter of an inch thick. (*Half-Yearly Abst.*, 1872, 108.)

Chemical Properties.

General Chemical Nature.—*Anhydrous sulphuric acid*, known also as *sulphuric anhydride*, is a compound of one atom of Sulphur with three atoms of Oxygen, SO_3, forming a white crystalline substance, apparently destitute of acid properties. It melts to a clear liquid at about 18° C. (65° F.), and boils at about 46° C. (115° F.), being dissipated in the form of a colorless vapor. It has an intense affinity for water, with which it unites with violence, forming the ordinary hydrated acid.

The most concentrated form in which this acid is found in commerce is usually a definite chemical combination of one molecule of the so-called anhydrous acid with one molecule of water, H_2O, $SO_3 = H_2SO_4$. In this state, when pure, it is a colorless, odorless, highly acrid, corrosive, oily liquid, having a specific gravity of 1.845, and containing 81.6 per cent. of the anhydrous acid; it boils at a temperature of 327° C. (620° F.), and freezes at —34° C. (—29° F.). In certain respects this hydrated compound is the most powerful acid known. It has a strong attraction for water, which it readily absorbs from the atmosphere; it mixes with this liquid in all proportions, with a contraction of volume, and the evolution of much heat. In proportion as it is mixed with water it loses its oily consistency and becomes specifically lighter; when diluted to a density of 1.5 its oily appearance will have about disappeared, and it will have a less energetic action upon organic substances. The density of the diluted liquid, when pure, indicates the amount of real acid present.

The following table, abridged from that first constructed by Dr. Ure, indicates the percentage by weight of anhydrous (SO_3) and of

monohydrated acid (H_2SO_4), in pure solutions of different specific gravities:

STRENGTH OF AQUEOUS SOLUTIONS OF SULPHURIC ACID.

Specific Gravity.	Percentage of		Specific Gravity.	Percentage of		Specific Gravity.	Percentage of	
	SO_3.	H_2SO_4.		SO_3.	H_2SO_4.		SO_3.	H_2SO_4.
1.848	81.54	100	1.539	53.00	65	1.218	24.46	30
1.837	77.46	95	1.486	48.92	60	1.179	20.38	25
1.811	73.39	90	1.436	44.85	55	1.141	16.31	20
1.767	69.31	85	1.388	40.77	50	1.101	12.23	15
1.712	65.23	80	1.344	36.69	45	1.068	8.15	10
1.652	61.15	75	1.299	32.61	40	1.033	4.08	5
1.597	57.08	70	1.257	28.54	35	1.007	0.81	1

The acid of commerce has frequently a dark-brown color, due to its having been brought in contact with organic matter. Sulphuric acid quickly chars animal and vegetable substances; when dropped, even in a much diluted state, on black woollen cloth, it causes it to assume a red color, which after a time fades to brown. Many substances, such as certain metals, charcoal, and various organic compounds, when heated with the concentrated acid, decompose it with the evolution of sulphurous acid gas (SO_2). In a diluted state, in the presence of some of the metals, such as zinc, it decomposes water, at the ordinary temperature, with the evolution of hydrogen gas and the formation of a salt of the metal.

The *salts* of sulphuric acid are usually colorless, and for the most part readily soluble in water. The sulphates of the fixed alkalies and of the alkaline earths are unchanged by a red heat, but most other sulphates readily undergo decomposition when strongly ignited. When thoroughly mixed and ignited with either charcoal or a mixture of carbonate of sodium and cyanide of potassium, or with ferrocyanide of potassium, all metallic sulphates are readily decomposed with the formation of a sulphide of the metal. This residue, when acted upon by hydrochloric acid, evolves sulphuretted hydrogen gas, with the formation of a chloride of the metal.

Special Chemical Properties.—When in its concentrated state, sulphuric acid may be readily recognized by the properties already mentioned, such as its carbonizing action on organic matter, evolving heat when mixed with water, etc.; but when in a diluted

state, its presence has to be determined by other tests. The acid has the property of reddening veratrine, piperine, phloridzine, oil of bitter almonds, and several other organic compounds. On account of the solubility of most of the compounds of sulphuric acid, there are but few reagents that precipitate it from solution; however, there is no substance that can be detected with greater certainty and ease than this acid.

The presence of free sulphuric acid in solution with a sulphate may be recognized by adding a little cane sugar and evaporating the mixture to dryness at 100° C. (212° F.), when, if the free acid be present, the residue has a black color, due to the charring action of the acid; if only a trace of the free acid be present, the residue will have a blackish-green color. No other free acid behaves in this manner with cane sugar (Runge).

In the examination of the following tests, aqueous solutions of pure sulphuric acid were chiefly employed. The fractions refer to the amount of monohydrated sulphuric acid (H_2SO_4) present in one grain of the solution; and the results, unless otherwise stated, to the behavior of one grain measure of the solution.

Chloride of Barium.

Barium chloride and barium nitrate produce in solutions of free sulphuric acid, and of its salts, an immediate white precipitate of barium sulphate, $BaSO_4$, which is insoluble in free acids and in the caustic alkalies. In applying this test to neutral solutions for the detection of combined sulphuric acid, the solution should first be acidulated with either hydrochloric or nitric acid.

1. $\frac{1}{100}$ grain of monohydrated sulphuric acid in solution in one grain of water yields with either of the above reagents an immediate, copious precipitate, which, if the mixture be not much agitated, consists of feathery stellate crystals, needles, and granules, Plate II., fig. 4. The same crystalline deposit may be obtained from the acid when in solution in the form of a sulphate; at least from the sulphates of potassium, sodium, magnesium, and copper. If the mixture be much agitated on the addition of the reagent, the precipitate is wholly in the form of very small granules. The precipitate, whether crystalline or otherwise, remains unchanged on the addition of several drops of concentrated hydrochloric acid.

2. $\frac{1}{1000}$ grain yields a rather copious, principally amorphous but partially granular precipitate.
3. $\frac{1}{5000}$ grain: an immediate amorphous deposit.
4. $\frac{1}{10,000}$ grain: after a very little time there is a very good precipitate. A drop of the sulphuric acid solution immediately reddens litmus-paper.
5. $\frac{1}{25,000}$ grain: an immediate turbidity, and, after a little time, a very satisfactory deposit. A drop of this solution faintly reddens litmus-paper.
6. $\frac{1}{50,000}$ grain: very soon the mixture is distinctly turbid, and after several minutes it yields a quite distinct precipitate. This solution just perceptibly changes the color of normal litmus-paper.
7. $\frac{1}{100,000}$ grain: after some minutes a distinct deposit, which is usually, especially when nitrate of barium is employed as the reagent, granular.
8. $\frac{1}{200,000}$ grain: in about one minute there is a perceptible turbidity, which after several minutes becomes quite distinct.
9. $\frac{1}{400,000}$ grain yields, after from ten to fifteen minutes, a just perceptible cloudiness. This result is equally produced by either of the barium reagents.

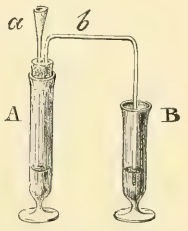
The last-mentioned quantity of sulphuric acid would form the 1–168,000th of a grain of barium sulphate. It is obvious, therefore, especially as there was some fluid added with the reagent, that this salt requires more than 168,000 times its weight of water for solution. There has been much discrepancy among observers in regard to the limit of this test, and the solubility of the barium compound. Thus, Harting placed the limit for chloride of barium at one part of anhydrous sulphuric acid in 75,000 parts of water; while Lassaigne placed it, for nitrate of barium, at one part of the acid in 200,000 parts of water, after from ten to fifteen minutes. (*Gmelin's Handbook*, vol. ii. 177, 192.) Again, Gmelin states (upon the authority of Klaproth?) that the sulphate of barium is soluble in 43,000 parts of water (*Handbook*, iii. 152); whereas Bischof concludes from his experiments (*Chem. and Phys. Geol.*, i. 450) that this salt requires something more than 209,424 times its weight of water for solution.

Confirmation of the Test.—If the sulphate of barium precipitated by this reagent be dried, then thoroughly mixed with about twice

its weight of powdered charcoal or of a well-dried mixture of equal parts of sodium carbonate and potassium cyanide, and the mixture heated to redness, for convenience on platinum-foil, the barium salt yields up its oxygen and becomes reduced to sulphide of barium (BaS). This same conversion may be effected in a similar manner by ferrocyanide of potassium, as first advised by Dr. E. Davy for the reduction of arsenical compounds; the salt should be previously pulverized and thoroughly dried at 100° C. (212° F.) in a water-bath. Before using either of these reducing agents for the reduction of the barium precipitate, a portion of the agent should be ignited alone, and then tested for a sulphide, in the manner about to be described: this precaution is necessary, since the reducing agent itself might contain a sulphate. In the absence of platinum-foil or a small platinum or porcelain crucible, the ignition of the sulphate mixture may be performed in an ordinary reduction-tube.

The presence of a sulphide in the ignited sulphate mixture may be shown by moistening the cooled residue with diluted hydrochloric acid, when it will evolve *sulphuretted hydrogen* gas. The presence of this gas may be recognized by its peculiar odor, and by its imparting a brown color to a slip of bibulous paper previously moistened with a solution of acetate of lead and exposed to it. Or, the evolved gas may be conducted into a solution of acetate of lead, when it will produce a black precipitate of lead sulphide, or at least impart a brown coloration to the solution. For this purpose, the cooled residue is placed, with a few drops of water, in a small test-tube, Fig. 1, A, and treated with a few drops of hydrochloric acid, added by means of a small funnel-tube, *a*; the evolved gas is conducted through a delivery-tube, *b*, into a few drops of the lead solution, acidulated with acetic acid, contained in a second test-tube, B. By blowing through the funnel-tube of the apparatus, the last traces of the evolved gas will be brought in contact with the lead solution. By this method, the sulphuretted hydrogen evolved from the 1–100th of a grain of sulphuric acid will produce a distinct precipitate, and from the 1–1000th of a grain, a distinctly brown coloration.

Fig. 1.



Apparatus for detection of sulphide of barium.

So, also, the ignited residue may be placed on a piece of paper which has previously been saturated with a lead solution and nearly

dried, and then touched with a drop of diluted hydrochloric acid, when the moistened paper will assume a brown color; or, it may be placed in a watch-glass and moistened with the acid, and another similar glass, containing a fragment of paper moistened with the lead solution, inverted over this. By either of these methods, especially the latter, the most minute traces of a sulphide will manifest themselves.

Fallacies.—Solutions of salts of barium also produce white precipitates in solutions of *Selenic* and *Hydrofluosilicic* acids, even in the presence of other free acids. Both these substances are very rare, and only possible to be met with in medico-legal investigations. The fluorine precipitate, at least from strong solutions, is crystalline; but the form of the deposit, Plate II., fig. 4, readily distinguishes it from the sulphate precipitate. The *selenate* of barium is amorphous. This salt is soluble in hot hydrochloric acid, with the evolution of free chlorine; but the silico-fluoride of barium is almost wholly insoluble in either hydrochloric or nitric acid. Solutions of selenic acid, like those of sulphuric acid, yield precipitates when treated with soluble salts of strontium and of lead; but the fluorine acid forms no precipitate with solutions of these metals. The precipitate from either of these acids would not, of course, yield a sulphide upon ignition with a reducing agent.

In applying this test it must also be borne in mind that when relatively large quantities of strong solutions of chloride of barium, and of barium nitrate, are added to a liquid containing much free hydrochloric acid or free nitric acid, it may yield a white precipitate of the reagent salt, since these salts are less soluble in a strong solution of either of these acids than in pure water. Under these circumstances, however, the precipitate would readily disappear on the addition of water; whereby it would be distinguished from the barium sulphate.

When the reagent is added to *neutral* or *alkaline* solutions, it produces white precipitates with several acids other than those already mentioned, such as carbonic, phosphoric, oxalic, etc.; but the precipitate produced from either of these, unlike the sulphate of barium, is readily soluble in hydrochloric and nitric acids.

2. *Nitrate of Strontium.*

This reagent produces in solutions of free sulphuric acid, and of

its salts, a white precipitate of strontium sulphate, $SrSO_4$, which is quite perceptibly soluble in hydrochloric and nitric acids, and much more soluble in water than the corresponding barium compound. From dilute solutions the formation of the precipitate is much promoted by warming the mixture, and also by agitating it with a glass rod.

If the precipitate be collected and ignited with charcoal, or any other reducing agent, it leaves a residue of sulphide of strontium, which may be recognized as such in the same manner as the sulphide of barium.

1. $\frac{1}{100}$ grain of free sulphuric acid, in one grain of water, yields with the reagent a rather copious crystalline precipitate, consisting of groups of exceedingly delicate transparent needles, and granules, Plate II., fig. 6. The granules are somewhat larger than those produced by the barium reagent. The deposit remains unchanged on the addition of a few drops of hydrochloric acid. Similar results are obtained from the acid when in solution in the form of a sulphate.
2. $\frac{1}{1000}$ grain: an immediate cloudiness, and very soon a quite good granular deposit.
3. $\frac{1}{5000}$ grain: in about one minute there is a perceptible cloudiness, and in a few minutes a good granular precipitate.
4. $\frac{1}{10,000}$ grain: after a few minutes a distinct turbidity, and after several minutes a quite satisfactory deposit. The separation of the precipitate is much hastened by agitating the mixture.
5. $\frac{1}{20,000}$ grain, yields after several minutes a just perceptible cloudiness, which increases but little, even after half an hour.

Wackenroder states that the sulphate of strontium dissolves slowly but completely in a solution of common salt, in which respect it differs from the corresponding salt of barium.

The reaction of this test is subject to about the same *fallacies* as the preceding reagent.

3. *Acetate of Lead.*

Solutions of free sulphuric acid and of sulphates yield with this reagent a white amorphous precipitate of sulphate of lead, $PbSO_4$, which is sparingly soluble in dilute hydrochloric and nitric acids. It is somewhat soluble in solutions of the caustic alkalies, as also in some of the salts of ammonia.

1. $\frac{1}{100}$ grain of the acid yields a copious amorphous precipitate, which in a large measure is dissolved on the addition of a single drop of concentrated hydrochloric acid.
2. $\frac{1}{1000}$ grain: a rather copious precipitate, which, on the addition of a drop of hydrochloric acid, very nearly all disappears.
3. $\frac{1}{10,000}$ grain yields an immediate turbidity, and in a few minutes a very satisfactory deposit.
4. $\frac{1}{20,000}$ grain: after some minutes a just perceptible turbidity, which increases but little on standing.

This test is subject to many more fallacies than either of the tests already mentioned.

4. *Veratrine.*

Veratrine, when added to a drop of *concentrated* sulphuric acid, slowly assumes a yellow color and in a little time dissolves to a beautiful crimson-red solution. This solution is produced immediately by warming the mixture. In the diluted acid, the alkaloid dissolves slowly without change of color.

1. $\frac{1}{100}$ grain: when a small quantity of the alkaloid is introduced into one grain of a 1–100th solution of the *free* acid and heat applied, it dissolves to a colorless mixture, which, when evaporated to dryness on a water-bath, leaves a beautiful crimson-colored deposit.
2. $\frac{1}{1000}$ grain of the acid, when treated in a similar manner, leaves a residue, the border of which has a fine crimson color.
3. $\frac{1}{5000}$ grain: the residue has a just perceptible red tint, which, however, is not well marked.

Since this reagent produces no coloration with neutral sulphates, it serves to distinguish the uncombined acid from these salts. And for this purpose we recommend it as much superior in every respect to the cane-sugar method of Runge. A drop of a saturated solution of the neutral sulphate of either of the fixed alkalies and of other similar salts, when treated with the alkaloid and evaporated to dryness, failed to produce any red coloration whatever.

This reaction is peculiar to the acid in question.

Other Reactions.—*Chloride of Calcium* produces in somewhat concentrated solutions of free sulphuric acid and of its salts a white, granular, but sometimes crystalline, precipitate of calcium sulphate, which slowly disappears on the addition of water, it being rather

freely soluble in this fluid. One grain of a 1–100th solution of the free acid yields only a slight turbidity.

Metallic copper, when present in strong, boiling solutions of sulphuric acid, decomposes it, with the evolution of sulphurous acid gas (SO_2), which may be recognized by its peculiar odor and its bleaching properties. This decomposition, however, does not occur when the acid is diluted with as much as about ten times its weight of water. So, also, when not too dilute, the acid decomposes, at ordinary temperatures, the sulphide of iron, with the evolution of sulphuretted hydrogen gas, known by its peculiar odor and its action on salts of lead. When the acid contains about twenty-five times its weight of water, the decomposition takes place very slowly; and when but little more diluted, not at all. This decomposition, however, is common to several other acids.

Separation from Organic Mixtures.

Suspected Solutions.—If the solution presented for examination be some article of drink, food, or medicine having a strong acid reaction, and free from mechanically suspended matter or solids, the tests for sulphuric acid may be applied at once, even though the liquid be highly colored. For this purpose, a *given portion* of the solution, after concentration if necessary, is treated with a solution of chloride of barium as long as it produces a precipitate. The mixture is then warmed, and the deposit collected on a filter, well washed with water containing pure hydrochloric acid, and dried. If the mixture containing the precipitate be so strongly acid that it perforates the filter, the latter is supported on a muslin cloth, or the solution is diluted before filtration.

When an organic mixture thus yields with chloride of barium a white precipitate which is insoluble in hydrochloric acid, there is scarcely a doubt of the presence of sulphuric acid, either free or otherwise. It is more satisfactory, however, to ignite a portion of the dried precipitate with a reducing agent and determine the presence of a sulphide in the residue, in the manner already pointed out. When this examination yields positive results, there is no longer any doubt whatever of the presence of the acid. The reactions of this test may, however, be confirmed by examining other portions of the solution by some of the other tests for the acid.

If the mixture presented for examination contains much solid organic matter, it should, after dilution if necessary, be kept at a boiling temperature for ten or fifteen minutes, then, when cooled, filtered, and the solids on the filter well washed with warm water. The filtrate thus obtained is properly concentrated and examined in the manner just described.

Although in this manner the *presence* of sulphuric acid may be fully and unequivocally established, yet it does not follow that it was present in its *free* state, even when the liquid had a strong acid reaction. For it may have existed in the form of one of the acid sulphates, such as common alum, the solutions of which have an acid reaction; or it may have been present as a neutral sulphate, such as sulphate of magnesium, and the acidity of the mixture have been due to the presence of some other acid, as acetic acid in the form of vinegar; or, lastly, only a portion of it may have been free, the mixture having contained both the free acid and a sulphate.

To determine this point, a portion of the suspected solution is evaporated to dryness, when, if it leaves no saline residue or only an insignificant one, it is certain that the acid existed in its free state; if, however, it leaves a saline deposit, then there may have been no free sulphuric acid present. When the original mixture contains much organic matter, it may be difficult at first, by simple inspection, to determine the presence or otherwise of saline matter in the evaporated residue. When this is the case, the residue should be moistened with pure nitric acid and the mixture evaporated at a moderate heat to dryness, and the operation repeated until the dry residue has a yellow color, after which the heat is gradually increased till the organic matter is entirely destroyed, when, if a salt be present, it will remain as a white mass. The nitric acid in this operation facilitates the decomposition of the organic matter, and at the same time prevents the reduction of any sulphate present to the state of sulphide, which might otherwise take place during the oxidation of the organic matter. If the ignited mixture thus leaves a saline residue, a portion or the whole of the sulphuric acid *may* have existed in the form of a sulphate. A portion of the residue may be dissolved in water and the solution tested in the ordinary manner. It does not follow, however, from thus obtaining a sulphate, for reasons pointed out hereafter, that even any part of the acid originally existed in its combined state; yet, under these circumstances, it can never be proved

by chemical means that the *whole* of the acid was originally present in its free state.

For determining and separating free sulphuric acid from solutions of its salts various methods have been advised. Thus, it has been proposed to concentrate the mixture to near dryness and agitate the residue with absolute alcohol or ether, for the purpose of dissolving the free acid while its salts would remain insoluble. But, as remarked by Dr. Christison, alcohol will extract a portion of sulphuric acid from acid sulphates, and even neutral sulphates are not wholly insoluble in this menstruum; and again, ether extracts the free acid only to a very limited extent, even in the presence of only a very minute quantity of water. It has also been proposed to add to the warmed mixture finely-powdered barium carbonate, in small quantity at a time, as long as it produces effervescence, by which the free acid would be precipitated as barium sulphate, while the soluble sulphate present would remain unacted upon. The precipitate thus obtained would, therefore, represent the amount of free acid present. By stopping the addition of the barium carbonate the moment effervescence ceases, this method, under certain conditions, yields very accurate results; yet, if the sulphate present was a neutral alkaline salt, it would, partially at least, be estimated as an acid sulphate, while, on the other hand, some of the acid sulphates, as common alum, decompose carbonate of barium with effervescence. Should, however, the original mixture contain a sulphate and a free acid not sulphuric, the operator might be wholly misled by this method. Thus, if the free acid existed in excess over the salt, the carbonate of barium would precipitate the whole of the sulphuric acid from the salt, and still give rise to effervescence: under these circumstances, therefore, the whole of the precipitate would be due simply to the presence of a sulphate.

When the examination has shown the presence of sulphuric acid in a solution which contains a saline compound, the safest and most accurate method for determining whether or not the whole of the acid may have existed in the form of a sulphate is the following: A given volume of the solution, after the addition of a little hydrochloric acid, is treated with excess of chloride of barium, and the precipitate collected, dried and weighed, in the manner described hereafter; an equal volume of the solution is then evaporated to dryness, the residue thoroughly dried, but not ignited, then dissolved

in acidulated water, the filtered solution precipitated as before, and the dried deposit weighed. Every 2.38 parts by weight of the former precipitate in excess over the latter correspond to one part of free monohydrated sulphuric acid. This estimate may, however, fall short of the real amount of the free acid originally present, but it could never exceed it. If, in determining the amount of combined acid in the evaporated residue, the latter be ignited, any acid sulphate present might give up a portion of its acid, which would, therefore, be estimated as free; so, also, the ignition might reduce some of the sulphate to the state of sulphide, and thus cause an error in the same direction. If the suspected solution contained simply a sulphate and a free acid other than sulphuric, the precipitates obtained by both of the above operations would, of course, be equal in weight.

Although this method, as just intimated, may, under certain conditions, fail to show the whole of the acid as free that really existed as such, yet in most instances this would not be likely to affect seriously the results. Nevertheless, cases might occur in which the operator would be led to conclude that little or even none of the acid was present in its free state, when the whole of it had been added as such. Thus, for example, if free sulphuric acid was added to a solution of chloride of sodium, or common salt, the mixture on evaporation would leave an acid sulphate of sodium, the chlorine, in part at least, of the common salt being expelled in the form of hydrochloric acid. If, under these circumstances, the amount of salt present equalled or exceeded the acid added, the whole of the latter would be estimated as combined. Similar results would be observed in regard to solutions of other salts. In a solution containing one base and two different acids, especially in about equivalent proportions, it is impossible by chemistry alone to determine which acid originally existed in combination with the base. Cases of this kind, it is true, are not likely to occur in medico-legal investigations, especially in the examination of suspected articles of food or drink, yet it is well to bear in mind the possibility of their occurrence. In suspected solutions containing this poison, the nature of the mixture and attending circumstances usually leave no doubt as to its true character.

Contents of the Stomach.—These, carefully collected in a large porcelain dish, are tested in regard to their chemical reaction, any solids present cut into small pieces, and the mixture, after the addition

of water if necessary, kept at about a boiling temperature for half an hour or longer; the cooled mass is then strained, the solids washed with hot water, the united liquids concentrated, filtered, and the filtrate examined in the manner pointed out above. This method would, of course, be equally applicable for the examination of the matters ejected from the stomach by vomiting during life. Should an antidote, such as an alkaline carbonate, have been administered, the contents of the stomach, as well as the matters vomited, may contain the acid only in the form of a sulphate and have a neutral reaction. Under these circumstances, in the preparation of the mixture, it should be strongly acidulated with hydrochloric acid; the amount of combined sulphuric acid is then estimated in the manner already described.

So, also, if the person had been actively treated or survived the taking of the poison some days, it may have *entirely* disappeared from the stomach. This result has been observed in several instances in which death took place within even short periods. Thus, in a case mentioned by Mertzdorff, in which the acid proved fatal within twelve hours to a child, the contents of the stomach had no acid reaction, but, on the contrary, an ammoniacal odor, and contained a soluble sulphate, probably the sulphate of ammonium. (*Christison On Poisons*, 126.) This conversion, according to Orfila, always takes place with greater or less rapidity when the acid is present in decomposing nitrogenized organic mixtures. M. Buchner mentions five instances of fatal poisoning by this acid and nitric acid, in which there was a failure to detect the presence of the acid after death. (*Jour. Chim. Méd.*, 1867, 179.)

It is well known that the natural secretions of the stomach have usually a distinctly acid reaction, due to the presence of minute quantities of hydrochloric and lactic acids. Whether the acidity of the mixture under examination is due simply to these acids or really to the presence of free sulphuric acid, can, of course, be determined only by the attending circumstances and a chemical analysis. In determining the quantity of free sulphuric acid present, it must be borne in mind that the contents of the stomach usually contain small quantities of alkaline salts, particularly chlorides, and that these, on evaporating the mixture to dryness, will convert a corresponding portion of the free acid into sulphates: the proportion thus converted, however, would rarely affect the general results. In this connection

it must also be remembered that sulphates may be normally present in very minute quantity in articles of food and complex organic mixtures; and, moreover, that some of these salts are used medicinally in large doses.

From the above considerations, it is evident that in poisoning by sulphuric acid cases may readily arise in which the proof of the poisoning will rest chiefly or entirely upon the symptoms and *post-mortem* appearances. In all such cases, however, we should be able to account satisfactorily for the failure of the chemical analysis.

From organic fabrics.—The texture of articles of clothing with which sulphuric acid comes in contact is usually more or less destroyed, and the spots remain moist for a long period, due to the affinity of the acid for water; so, also, the color of the article is more or less changed, it in most instances assuming a reddish or brownish hue. These spots may retain an acid reaction for many months or even years.

The presence of the acid in stains of this kind may be determined by boiling the stained portion with a small quantity of pure water, filtering the solution thus obtained, and examining the filtrate in regard to its chemical reaction and with chloride of barium, in the usual manner. A portion of the filtrate should also be examined in regard to the presence of saline matter. Should the latter be present with the acid, it then becomes necessary to determine, in the manner already indicated, whether or not the whole of the acid may have been in its combined state. If the examination shows that this may have been the case, it is then necessary to examine an equal portion of the unstained article, after the same process, since in the preparation of fabrics of this kind minute quantities of sulphates are sometimes employed.

Quantitative Analysis.—Sulphuric acid is usually estimated in the form of sulphate of barium. For this purpose the solution is treated with slight excess of chloride of barium, and the mixture gently heated until the barium precipitate has completely subsided. The deposit is then collected on a small filter of known ash, repeatedly washed with hot water containing hydrochloric acid, dried, ignited, and weighed. When only a small quantity of the precipitate is present, after being washed and dried it should as far as practicable be removed from the filter and ignited alone; the

filter with any adherent sulphate is then ignited, and the weight of the residue, after deducting the ash of the filter, added to the weight of the previously ignited sulphate.

Every one hundred parts by weight of barium sulphate thus obtained correspond to 42.06 parts of monohydrated sulphuric acid, 105 grains of which measure one fluid-drachm.

Section II.—Nitric Acid.

Nitric Acid, or *aqua fortis*, as found in the shops, is a powerfully corrosive acid liquid, having usually a more or less yellow or even reddish color. In its action upon organic substances it is about equally active with sulphuric acid. Instances of poisoning by it, however, have been of very much less frequent occurrence than by the latter.

Symptoms.—These in most respects are identical in kind with those observed in sulphuric acid poisoning. When the acid is swallowed in its concentrated state, the mucous membrane of the mouth and other parts with which the liquid comes in contact is immediately corroded and assumes a white appearance, which, however, unlike that produced by sulphuric acid, soon changes to yellow, and then in some instances slowly becomes more or less brown. All spots produced on the external skin by the acid very soon acquire a permanent yellow color.

The usual symptoms are violent pain in the mouth, œsophagus, and stomach; copious eructations of gaseous matter, having sometimes a reddish color, due to the presence of the decomposed acid; excessive vomiting of strongly acid, yellow or brownish matters; tenderness and tension of the abdomen; general coldness of the body, especially in the extremities; difficulty of respiration and of deglutition, from the local action of the acid on the internal organs of the mouth and fauces; a small and frequent pulse; extreme thirst, cold sweats, and great prostration of strength. The local action of the acid may be confined to the mouth and fauces, none of the poison having been swallowed.

In most instances the more immediate symptoms produced by nitric acid are proportionate to the degree of its concentration and the quantity taken; but this is by no means always the case. Thus, Dr. Beck cites the case of a young man who died in twenty hours, from the effects of the acid, without at any time showing signs of

acute pain or of agitation; yet after death there was found perforation of the stomach, with great effusion of its contents into the abdomen. In another case, a woman swallowed a quantity of the poison, and, at least for some hours afterward, there was neither agitation, pain, nor vomiting, but a condition rather indicating typhus fever. She died the following day, and on examination of the body there was found most extensive disorganization of the abdominal organs: perforation of the stomach, gangrenous spots, effusion into the abdomen, marked erosion, and a general yellow color of all the viscera.

In a case reported by Dr. Stevenson (*Guy's Hosp. Rep.*, 1872, 223), a man, aged twenty-one, swallowed with suicidal intent three fluid-ounces of nitric acid, of the ordinary strong commercial preparation. Although magnesia was given as an antidote, the man died seventeen hours after taking the poison, after the ordinary symptoms of poisoning by the mineral acids, but he suffered much less pain during the last few hours of life than during the period more immediately following the taking of the acid.

If the patient survive the primary effects of the poison, these may be succeeded by irregular fever, obscure pains in the throat and epigastric region, impaired digestion, irritability of the stomach, frequent vomiting, obstinate constipation, dryness of the skin, disturbed respiration and deglutition, sometimes profuse salivation, fetid breath, frequent rigors, and great muscular emaciation. Sometimes large membranous flakes, or even masses of the lining membrane of the throat and œsophagus, are ejected with the vomited matters.

The *vapor*, or *fumes*, arising from nitric acid has in several instances caused death. In an instance of this kind, a chemist, Mr. Stewart, of Edinburgh, and his assistant inhaled the fumes while endeavoring to save a portion of the liquid that had escaped from a broken jar. After an hour or two, the former began to experience difficulty of breathing, and sent for medical advice, but he very rapidly became worse, and died in about ten hours after the accident. His assistant was also taken ill, and died about fifteen hours later. (*Chem. News*, London, March, 1863, 132.) An instance is also reported by Mr. Spence, in which the fumes of the acid proved fatal to two persons; the first of whom died in about forty hours, and the other some hours afterward. (*Ibid.*, 167.) In at least one of these cases the symptoms were delayed for some hours. In still

another case, a man spilled some nitric acid from a carboy, and in endeavoring to collect it he inhaled enough of the vapor to cause his death. (*New Remedies*, 1880, 32.) In the well-known case of Mr. Haywood, who inhaled the fumes arising from a mixture of nitric and sulphuric acids, the symptoms were delayed for more than three hours, and death occurred in about eleven hours.

Period when Fatal.—Nitric acid has in several instances caused death within a very few hours, and in most instances in which death occurred from its primary effects, that event followed within forty-eight hours; but the patient may recover from the primary action of the poison and die from secondary effects many months afterward. Thus, in a case quoted by Dr. Taylor, death occurred in *one hour and three-quarters* after the poison had been swallowed; while, on the other hand, Tartra mentions an instance in which death did not occur until after a period of *eight months;* and another is reported in which the patient survived *six months.* Out of fifty-six cases of poisoning by nitric acid, collected by Tartra, twenty-one of the patients completely recovered, and eight partially.

Fatal Quantity.—In most of the instances of poisoning by this substance, the quantity taken was not ascertained. Most writers on this subject, however, agree in fixing the fatal quantity, for a healthy adult under ordinary conditions, at about *two drachms* of the concentrated acid; yet quantities much larger than this have in several instances been followed by complete recovery. In a case reported by Dr. J. M. Warren, a woman, aged thirty-four years, having with suicidal intent taken three drachms of the acid into her mouth, swallowed a portion, but most of it was spit out. She was seized with the usual symptoms, which, however, after several days, under active treatment, nearly subsided; but secondary symptoms set in, and she died on the fourteenth day after the poison had been taken. (*Amer. Jour. Med. Sci.*, July, 1850, 36.) A boy two years old took into his mouth a drachm of fuming nitric acid. He at once spat it out, and recovered from its local effects.

Treatment.—This consists in the speedy administration of calcined magnesia, chalk, or a dilute solution of an alkaline carbonate, followed by the free exhibition of oily or mucilaginous drinks. In every respect, the treatment is the same as that already mentioned in sulphuric acid poisoning (*ante*, 101).

Post-mortem Appearances.—These will, of course, depend

somewhat on the length of time the individual survived after taking the poison. In *acute* cases, the lining membrane of the lips, mouth, and fauces has sometimes a white, but more generally a deep yellow or even brownish color; often large patches of this membrane are entirely removed. The mucous membrane of the œsophagus is often much thickened and altered in structure, of a yellow color, and readily separated. And like appearances may be observed in the larynx and trachea, if the acid has passed into these organs. In these examinations, as in sulphuric acid poisoning, it must be borne in mind that the mouth and œsophagus may exhibit but little injury, the stomach being the part chiefly affected; and, on the other hand, that the whole of the local injury may be confined to the mouth and air-passages, little or none of the poison having been swallowed. In an instance of poisoning by this acid quoted by Dr. Christison, it left no trace of its passage downward until it had arrived near the pylorus.

The stomach is usually distended, externally changed in color, more or less inflamed, and adherent to the neighboring organs. The contents of this organ have frequently a yellow color, due to the action of the acid upon the contained matters. The mucous membrane is often greatly disorganized and much changed in color, and the blood-vessels are injected with dark coagulated blood. In the case reported by Dr. Warren, the stomach externally was of a purple color, and adherent to the neighboring parts; internally it was of a greenish-yellow color, and its tissues were so softened that it could not be separated from the surrounding parts without being greatly lacerated. When the coats of the stomach are perforated by the acid, —which, however, rarely happens,—the contents of the organ may escape into the abdomen and cause a yellow coloration and great disorganization of all the neighboring viscera.

The small intestines, particularly the upper portion, may exhibit appearances similar to those found in the stomach; often, however, they entirely escape the direct action of the acid, it not passing below the stomach. The large intestines are usually filled with hard fæces. The other abdominal organs are often more or less highly inflamed, even when the stomach is not perforated; the bladder is usually empty, no urine having been secreted.

In Dr. Stevenson's case, in which three ounces of the acid proved fatal in seventeen hours, the lips and angles of the mouth were found

discolored yellow, and also a portion of the tongue. Beyond this the mucous surface of the alimentary canal, as far as the stomach, was white, and covered with a thin paint-like coat of milky opacity. At the lower end of the œsophagus the mucous membrane was partly removed. The pharynx was much swollen, with its cavity somewhat narrowed. The larynx exhibited signs of decreasing inflammation from above downward. The stomach contained a small perforation on the anterior surface, half an inch from the lower border. Close around the perforation, the peritoneum was ecchymosed, but no lymph was exuded. The walls of the stomach were collapsed in stiffened folds, and at several points were nearly perforated. The gastric mucous membrane was covered with a deep reddish-brown gritty paste, which was neutral to litmus. The duodenum showed sloughing of the valvulæ conniventes. The jejunum and ileum were natural, but their contents consisted of tarry blood, especially in the ileum. The right side of the heart contained a clot of black blood.

When the patient survives the primary effects of the poison and dies from secondary results, the body is greatly emaciated, and the stomach and other portions of the alimentary canal are more or less contracted, their walls thickened and the cavities nearly closed. Stricture of the œsophagus has not unfrequently occurred, and the pyloric end of the stomach has been so greatly contracted as nearly to obliterate its opening. In some few instances, the stomach was so far destroyed that no part of its structure could be distinguished.

Chemical Properties.

General Chemical Nature.—*Anhydrous* nitric acid, or *nitric anhydride*, is a compound of the elements Nitrogen and Oxygen, in the proportion of two atoms of the former to five of the latter, N_2O_5. It is a transparent, colorless, crystalline solid; in this state it melts at 30° C. (86° F.), and boils at about 45° C. (113° F.): it was first obtained, in 1849, by Deville. In combination with water, it has long been known under the name of *aqua fortis*, which, in its most concentrated form, consists of one molecule of nitric anhydride in combination with one molecule of water, the combination forming two molecules of nitric acid, HNO_3; thus: $H_2O+N_2O_5=2HNO_3$.

In its pure state, nitric acid is a colorless, intensely corrosive acid liquid, which, in its most concentrated form, has a density of about 1.520, and contains 85.72 per cent. of the anhydrous acid. The density

of the acid of the shops usually varies from 1.350 to 1.450. Concentrated nitric acid is one of the most powerfully corrosive substances known. It imparts a yellow stain to the skin, nails, wool, and other organic substances. Exposed to the air, it emits white fumes; when mixed with water, it evolves a sensible amount of heat. It boils at about 84.5° C. (184° F.), and freezes at —40° C. (—40° F.). When the concentrated acid is boiled, it diminishes in density and its boiling point increases, until the liquid acquires a density of about 1.424, when it distils chiefly in the form of a hydrate of the acid, consisting of three molecules of water with two of the acid ($3H_2O$; $2HNO_3$).

The following table, according to Dr. Ure, indicates approximatively the percentage by weight of nitric anhydride, N_2O_5, in pure aqueous solutions of different specific gravities:

STRENGTH OF AQUEOUS SOLUTIONS OF NITRIC ACID.

Sp. Gr.	Percentage of N_2O_5.	Sp. Gr.	Percentage of N_2O_5.	Sp. Gr.	Percentage of N_2O_5.	Sp. Gr.	Percentage of N_2O_5.
1.500	79.7	1.402	56.6	1.258	35.1	1.117	16.7
1.491	76.5	1.383	53.4	1.246	33.5	1.093	13.5
1.479	73.3	1.363	50.2	1.221	30.3	1.071	10.4
1.467	70.1	1.343	47.0	1.196	27.1	1.048	7.2
1.453	66.9	1.322	43.8	1.183	25.5	1.027	4.0
1.439	63 8	1.300	40.4	1.171	23.9	1.016	2.4
1.419	59.8	1.283	38.3	1.146	20.7	1.005	0.8

Nitric acid as found in commerce is frequently more or less colored, the color being due to the presence of some of the lower oxides of nitrogen, and varying from a light yellow to an orange-red. In this state it is even more corrosive than the pure acid. It is not unfrequently contaminated with sulphuric and hydrochloric acids and other impurities.

The *salts* of nitric acid are for the most part colorless, and very freely soluble in water. They are all decomposed by a red heat. Their aqueous solutions are also decomposed when heated with free sulphuric acid, with the formation of a sulphate, the nitric acid being eliminated in its free state.

Special Chemical Properties.—Nitric acid very readily parts with a portion of its oxygen. When brought in contact with many of the metals, such as copper, zinc, iron, or tin, it is in part

decomposed with great rapidity, with the formation of a nitrate and the evolution of one or more of the lower oxides of nitrogen in the form of deep red fumes. The evolution of these fumes is quite characteristic of the acid.

When a nitrate, in its dry state, is brought in contact with ignited charcoal, the latter burns vividly at the expense of the oxygen of the nitric acid, the salt, if an alkaline compound, being converted into a carbonate.

On account of the free solubility of the compounds of nitric acid, it cannot be precipitated from solution by reagents; however, the presence of very minute traces of the acid can be detected with great certainty. When not too much diluted, it may be recognized by the properties already mentioned. In the following examination of the behavior of solutions of nitric acid, the fractions employed express the fractional part of a grain of *nitric anhydride* present in one grain of the solution.

1. *Copper Test.*

When tolerably strong nitric acid is treated in a test-tube with a slip of copper-foil, the acid is decomposed with the formation of copper nitrate, water, and the evolution of nitrogen dioxide, which latter on coming in contact with the air is oxidized, and escapes in the form of deep red fumes of nitrogen tetroxide; the copper nitrate thus formed imparts to the liquid a more or less greenish color. These reactions are expressed by the following formulæ: $8HNO_3 + Cu_3 = 3Cu\,2NO_3 + 4H_2O + N_2O_2$; and $N_2O_2 + O_2 = N_2O_4$.

When the acid is more dilute, it is not acted upon by copper unless the mixture be heated or free sulphuric acid be added, and the gas evolved may be colorless; its presence, however, may be recognized by its peculiar odor, acid reaction, and by rendering blue a piece of starch-paper moistened with a solution of iodide of potassium. In the presence of sulphuric acid, the whole of the nitric acid, whether in its free state or as a nitrate, is evolved finally in the form of nitrogen tetroxide.

The following results refer to the behavior of *five fluid-grains* of the nitric acid solution with a very small slip of copper-foil.

1. 1–10th solution, or half a grain of anhydrous nitric acid, fails to be acted upon by the copper till heat is applied,—then decomposition takes place quite briskly, yielding quite perceptible red

vapors, which quickly redden moistened litmus-paper, and impart a blue color to starch-paper prepared as above. The liquid assumes a very marked greenish-blue color.

2. 1–20th solution yields only a feeble reaction, even on the application of heat; but if a few drops of concentrated sulphuric acid be added, there is a brisk reaction, and ultimately the liquid acquires a very distinct greenish-blue color.
3. 1–50th solution gives no evidence of decomposition by heat alone; but with sulphuric acid and heat it yields a brisk reaction and a light greenish-blue solution. If this experiment be performed in a very narrow tube, the evolved gas imparts a distinct reddish hue to the contained air.
4. 1–100th solution, under the influence of a few drops of sulphuric acid and heat, yields a quite good effervescence around the surface of the copper, and the liquid acquires a faint greenish-blue color.
5. 1–500th solution, under the same influences as 4, yields a very distinct effervescence, and after a time the fluid acquires a perceptible greenish tint.
6. 1–1000th solution yields a perceptible reaction.

Results similar to the above may be obtained from the acid when in the form of a nitrate; but then the addition of sulphuric acid is necessary in all cases. If the nitrate to be tested is in the solid state, it should be dissolved in the least practicable quantity of water; on the other hand, if it is in solution, the liquid should be concentrated as far as practicable before the test is applied. In the use of this test, it must be kept in mind that sulphuric acid not unfrequently contains traces of nitric acid: the presence of this impurity could, of course, be determined by the test itself before it is applied to a suspected solution.

2. *Gold Test.*

If a solution of free nitric acid or of a nitrate be heated with excess of pure hydrochloric acid, the two acids react upon each other and eliminate free chlorine, which has the property of dissolving *gold-leaf* to the form of chloride of gold. The presence of the gold compound can be recognized, when present in not too minute quantity, by a solution of chloride of tin, which produces a purple precipitate, or at least imparts a purplish color to the liquid.

Before applying this test to a suspected solution, the hydrochloric acid about to be employed should be tested alone, in order to determine whether it is entirely free from uncombined chlorine, which is often present.

When *one grain* of the nitric acid solution is mixed, in a small test-tube, with five fluid-grains of tolerably strong hydrochloric acid and a *very small* slip of gold-leaf, the mixture on being heated to the boiling temperature yields the following results:

1. $\frac{1}{100}$ grain of nitric anhydride: in a very little time the gold dissolves; the cooled solution yields with the tin reagent no immediate change, but after a little time it assumes a decided purple color.
2. $\frac{1}{1000}$ grain: after a little time the gold dissolves, and the cooled solution yields with the tin compound a faint purple color.
3. $\frac{1}{5000}$ grain, after several minutes, dissolves a very minute quantity of gold; but the solution fails to yield satisfactory results with the tin reagent.

These reactions are also common to solutions of chlorates, hypochlorites, chromates, iodates, and bromates. The same is also true of the per-combinations of iron, as first pointed out by Henry Wurtz. (*Chem. Gaz.*, xvii. 32.) This metal is readily separated by treating the solution with sodium carbonate and filtration. It need hardly be added that a nitrate may be distinguished from all of these fallacious salts by the action of the preceding test.

3. *Iron Test.*

When free nitric acid, or a solution of a nitrate, is mixed with several times its volume of concentrated sulphuric acid and the *cooled* mixture treated with a crystal of sulphate of iron (*ferrous sulphate*), the latter after a time becomes surrounded by a blackish-brown, brownish, or purple compound, which is said to consist of $2FeSO_4$; NO, the reaction in the case of free nitric acid being: $2HNO_3 + 3H_2SO_4 + 10FeSO_4 = 3Fe_2 3SO_4 + 4H_2O + 2\,(2FeSO_4;\ NO)$.

Instead of using the iron salt in its solid state, it is more satisfactory to employ it in the form of a saturated solution. To thus apply the test, a drop of the nitric acid solution is thoroughly mixed in a small test-tube with eight or ten times its volume of sulphuric acid, the mixture gently warmed for a little time, then cooled by immersing the tube in cold water; a drop of the iron solution is

then allowed to flow down the inside of the tube upon the acid mixture, when the stratum where the two liquids are in contact will acquire a beautiful purple or brownish-purple color, the tint depending on the quantity of nitric acid present; on now slowly mixing the liquids by means of a glass rod, taking great care that no heat is evolved, the same coloration will be observed throughout the mixture.

1. $\frac{1}{100}$ grain of nitric anhydride, in one fluid-grain of water, when treated as above, the contact surfaces of the iron and acid liquids present a beautiful purple line; on carefully mixing the liquids, the mixture assumes a deep purple color, and soon begins to effervesce, gives out the odor of nitrogen tetroxide, and the color becomes discharged. On the addition of another drop of the iron solution, the color is reproduced.
2. $\frac{1}{1000}$ grain yields a beautiful purple mixture, which remains unchanged for at least several hours.
3. $\frac{1}{5000}$ grain: on mixing the two solutions, they assume a very decided purplish tint, which is permanent for some hours.
4. $\frac{1}{10,000}$ grain: the mixed liquids assume a distinct purplish hue, which after some hours becomes pinkish. These colors are best seen by inclining the tube over a piece of white paper.

Much the same results as those just described may be obtained by employing the iron compound in the solid state; its solution, however, is preferable. In all cases, before applying this test to a suspected solution, the sulphuric acid should be tested alone: in fact, it is somewhat difficult to find that acid in the shops entirely free from traces of nitric acid or some of the lower oxides of nitrogen.

4. *Indigo Test.*

When a solution of nitric acid, or of a nitrate, is mixed with hydrochloric acid or chloride of sodium, as recommended by Liebig, and the mixture colored by a solution of indigo, then heated with sulphuric acid, the chlorine set free through the agency of the nitric acid will discharge the blue color of the mixture. In applying this test, a small quantity of the nitric acid solution is treated with a few crystals of pure common salt or a drop of hydrochloric acid and just enough of a strong sulphuric acid solution of indigo to impart a distinct blue tint; the mixture is then heated, and while hot a few drops of concentrated sulphuric acid cautiously added and mixed with the

liquid, after which, if necessary, the heat is continued until the blue tint of the fluid disappears.

The following results refer to the behavior of *five grains* of the nitric acid solution.

1. 1–100th solution, when treated as above, the blue color, on the addition of a few drops of sulphuric acid to the heated mixture, is immediately discharged, and the liquid assumes a yellow color.
2. 1–1000th solution yields much the same results as 1.
3. 1–10,000th solution: the blue color is not discharged until the mixture is heated some minutes with several drops of sulphuric acid; the liquid then acquires a faint yellow tint.
4. 1–20,000th solution behaves much the same as 3.
5. 1–50,000th solution requires to be boiled several minutes with several drops of sulphuric acid before the blue tint disappears. For the success of this reaction it is necessary to employ the merest trace of indigo, the tint of which is best seen by inclining the tube containing the mixture over white paper.

It is well known that chlorates, chromates, iodates, binoxide of manganese, and several other similar compounds have, like nitric acid, the property of evolving chlorine from hydrochloric acid, and therefore of bleaching a solution of indigo; and Wurtz, in his valuable paper already referred to, has shown that the chlorides of gold, platinum, and tin bleach an indigo solution, even without the presence of hydrochloric acid, and that in the presence of this acid, arsenic acid has a similar property. It is not likely, however, that either of these fallacious substances would be present in a medico-legal investigation for nitric acid.

Much more probable sources of error than either of those just mentioned, to be guarded against, are the presence of free chlorine in the hydrochloric acid, and that of traces of nitric acid or some of the lower oxides of nitrogen in the sulphuric acid employed. No reliance whatever could be placed in this test when applied to organic mixtures.

5. *Brucine Test.*

This test, which was first suggested by Berthemont, is based on the production of a blood-red color when nitric acid or a nitrate is mixed with a sulphuric acid solution of brucine. Pure brucine, when added to *pure* sulphuric acid, assumes a pale pink color and

slowly dissolves to a colorless or nearly colorless solution, unless the proportion of alkaloid be comparatively large, when the solution has a pinkish hue.

When *one grain* of the free nitric acid solution or of a nitrate is mixed, for convenience in a white porcelain dish, with about *five fluid-grains* of concentrated sulphuric acid, and a few crystals of brucine added, if the solution contains:

1. $\frac{1}{100}$ grain of anhydrous nitric acid, the brucine immediately assumes a red-orange color, and, on being stirred, dissolves to a solution of the same hue, which very slowly fades to bright yellow.
2. $\frac{1}{1000}$ grain: the alkaloid acquires a red color, and yields a dull orange solution, which slowly becomes yellow.
3. $\frac{1}{5000}$ grain: the brucine assumes a rose-pink color, and dissolves to a solution having a decided reddish-pink hue, which changes to faint orange, then fades to yellow.
4. $\frac{1}{10,000}$ grain: the crystals acquire a pink color, and dissolve to a solution of the same tint, which becoming amber changes to yellow.
5. $\frac{1}{25,000}$ grain: the brucine assumes a reddish color, and, when stirred in the mixture, imparts to it a decided amber color, which soon changes to light yellow.
6. $\frac{1}{50,000}$ grain: the alkaloid becomes slightly colored, and yields a solution of a faint amber hue, which quickly changes to very light yellow. These colors are quite feeble, yet when the reaction is compared with that obtained from the alkaloid and sulphuric acid alone, the difference is very well marked.

When the nitric acid is in the solid state in the form of a nitrate, the reaction of this test is even more delicate than when applied to solutions. Under these circumstances, a very small portion of the salt, or the residue left on evaporating its solution to dryness, is dissolved in a few drops of sulphuric acid, and then a crystal or two of the alkaloid added. The residue obtained from a solution of potassium nitrate containing only the 1–100,000th of a grain of nitric acid, when moistened with a very small drop of sulphuric acid containing a little brucine, immediately assumes a distinct orange color, and dissolves to a brick-dust pink solution, the tint of which soon fades to faint yellow.

This test furnishes the most ready and delicate means of deter-

mining the purity of sulphuric acid in regard to the presence of traces of nitric acid.

A sulphuric acid solution of brucine also produces a somewhat similar coloration with chloric acid and its salts. But the most minute quantity of a salt of this kind imparts a strong yellow, and a very small quantity an orange color, to sulphuric acid alone, and evolves fumes of chlorine tetroxide, having a greenish color and peculiar odor. To guard against this fallacy, therefore, it is only necessary to observe the action of the sulphuric acid alone. But, besides this fallacy, there are certain other oxidizing agents that will produce with sulphuric acid and brucine a coloration similar to that caused by nitric acid.

6. *Narcotine Test.*

When a small quantity of narcotine is added to a few drops of pure concentrated sulphuric acid, the alkaloid dissolves to a light-yellow solution, which when heated assumes a purplish color; but if free nitric acid or a nitrate be present, the narcotine dissolves to a reddish-brown solution, which on the application of a gentle heat acquires a deep blood-red color. Mialhe was the first to employ this reaction as a test for nitric acid.

When one grain of the nitric acid solution is mixed with five fluid-grains of sulphuric acid, and the mixture allowed to cool, the addition of a few crystals of narcotine produces the following results:

1. $\frac{1}{100}$ grain of nitric anhydride: the alkaloid assumes a deep brown color, and imparts to the liquid a decided brownish-yellow color, which by heat is changed to a permanent deep blood-red.
2. $\frac{1}{1000}$ grain: the narcotine dissolves to a decided reddish solution, which when heated assumes a fine blood-red color.
3. $\frac{1}{5000}$ grain yields a distinct reddish color, which is changed to reddish-brown by heat.
4. $\frac{1}{10,000}$ grain: the solution of the alkaloid has a faint reddish tint, which by heat is changed to a purple-red. This last color might be readily confounded with that from narcotine alone; but this alkaloid singly would not impart the primary reddish tint.

When the nitric acid is in solution in the form of a nitrate, the liquid should be evaporated, and the *dry* residue dissolved in a few drops of colorless sulphuric acid, then tested by a few crystals of

narcotine. Under these conditions, given quantities of the acid yield even stronger colors than described above.

7. *Aniline Test.*

This test, first advised by M. Braun (*Jour. de Chim.*, 1867, 637), takes advantage of the production of a red color, due to the formation of fuchsine, when a drop of diluted nitric acid or of a nitrate is added to a mixture of a sulphuric acid solution of aniline and concentrated sulphuric acid.

The aniline solution may be prepared by dissolving one part of pure aniline, or its equivalent in the form of sulphate, in one hundred parts of a mixture of four parts of water and one part of concentrated sulphuric acid. A few drops of this solution are now added to about ten drops of pure concentrated sulphuric acid contained in a watch-glass or small porcelain dish, after which a drop of the nitric acid solution or a small fragment of solid nitrate is added to the mixture. Sooner or later fringes of a more or less intense red color make their appearance, and after a time the whole mixture acquires a more or less deep red color.

To obtain the best results by this test, it is necessary that the proportions of nitric acid and aniline present be within certain limits. In the presence of large excess of the acid, the color fails to appear, or is quickly discharged; whilst, on the other hand, in the presence of large excess of the aniline solution, the coloration is diminished in intensity. With a drop of a solution containing 1–100th of its weight or more of nitric acid, three or four drops of the aniline solution should be employed. Under proper conditions, the red coloration remains unchanged for many hours. The production of the red color is much facilitated, and the delicacy of the reaction increased, by gently warming the mixture.

1. $\frac{1}{100}$ grain of nitric anhydride soon produces, under the test, red or rose-red fringes, and after a time the mixture acquires a beautiful red coloration.

If, after the addition of the nitric acid, the mixture be warmed, immediately deep red fringes appear, and quickly the whole assumes a beautiful deep orange-red color.

2. $\frac{1}{1000}$ grain: on warming the mixture, quickly produces a rose-red coloration. Without the application of heat little or no color appears.

3. $\frac{1}{5000}$ grain: on warming the mixture, it quickly assumes a very distinct pinkish hue, which remains unchanged for some hours.
4. $\frac{1}{10,000}$ grain of nitric anhydride fails to impart to the warmed mixture any very distinct coloration.

The above results apply equally to nitric acid in its free state and when in the form of a nitrate. Under the action of the test, similar colorations are developed by hyponitrous and nitrous acids, and nitrites.

Chloric and *chromic* acids and their salts impart to the reagent mixture a deep *blue* color. In the case of chloric acid, the blue coloration appears even in the presence of 1–1000th grain of the acid; but with more minute quantities, even up to 1–10,000th grain, the mixture acquires a reddish or purple hue, which might be confounded with the reaction of minute quantities of nitric acid. But on gently warming the mixture, the reddish color produced by traces of chloric acid is quickly changed to blue; whereas the red color caused by nitric acid is much increased in intensity.

IODINE TEST.—This method, first proposed by J. Higgin (*Chem. Gaz.*, viii. 249), takes advantage of the property possessed by nitric acid of decomposing hydriodic acid with the evolution of free iodine, and the ready detection of the latter by means of starch. To apply this test, the suspected solution is mixed with about one-sixth of its volume of concentrated sulphuric acid and heated to near the boiling temperature for several minutes, then allowed to cool; the mixture is then treated with a drop of starch mucilage and a few drops of a very dilute solution of iodide of potassium, when, if nitric acid is present, the liquid acquires a more or less blue color. The author of this method states that a 1–20,000th solution of the acid yields in a few minutes a decided blue coloration. It must be remembered, however, that sulphuric acid alone will, after a time, liberate iodine, even from very dilute solutions of iodide of potassium.

OTHER TESTS.—Mr. J. C. Schaeffer has suggested a test, which depends on the conversion of nitric acid into nitrous acid by the action of metallic lead, and the production of a rich yellow color when the liquid is treated with potassium ferrocyanide and acetic acid. (*Chem. Gaz.*, ix. 289.) In somewhat strong solutions of the acid this reaction is well marked; but, as the reagent alone yields a

yellow coloration, it is not applicable for the detection of the acid when much diluted.

Mr. J. Horsley has proposed a test, which is applied as follows: A small quantity of water, acidulated with a few drops of sulphuric acid, is placed in a small test-tube, and a small portion of pyrogallic acid added, after which a little concentrated sulphuric acid is allowed to flow down the inside of the tube and subside to the bottom of the mixture; a few crystals of chloride of sodium are then added, and, after the effervescence has ceased, a small quantity of the solid nitrate to be examined is dropped into the mixture, when the subsided acid, in a very little time, assumes an intense purple or deep orange-brown color, which may ultimately extend throughout the entire mixture. (*London Chem. News*, June, 1863, 268.) We can confirm the statement of Mr. Horsley in regard to the extreme delicacy of this reaction, the smallest particle of a nitrate yielding a very satisfactory coloration.

Separation from Organic Mixtures.

Suspected Solutions.—If the suspected liquid has a strong acid reaction and is free from suspended solid matters, even though it is somewhat colored, a portion of it may be examined at once, by being placed in a small test-tube with a slip of copper, when if the fluid contains one-third or more of its volume of the ordinary nitric acid of the shops, it will immediately be acted upon by the metal, give off red fumes and yield a greenish-blue solution. If this reaction fail, the mixture, after the addition of sulphuric acid if necessary, is gradually heated, and any evolved gas examined in regard to its color, odor, and with wet litmus-paper and starch-paper moistened with a solution of iodide of potassium, in the manner already directed. A very good method of applying this test, when the quantity of liquid is limited, is to warm a few drops of the suspected solution with several drops of sulphuric acid and a slip of copper in a watch-glass covered by an inverted glass containing separate slips of the moistened litmus- and starch-papers. In applying this method, it must be remembered that when a sulphuric acid solution of a chloride is heated it will evolve hydrochloric acid gas, which also reddens litmus-paper; and if any oxidizing substance is present, a portion of the evolved acid may undergo decomposition with the elimination of free chlorine, which will blue moistened iodized starch-paper. If

there be any uncertainty in regard to the true nature of these results, a portion of the original solution is treated with a saturated solution of acetate of silver, when, if a chloride is present, it will yield a white precipitate of chloride of silver. If a precipitate be thus obtained, the solution is treated with slight excess of the silver reagent, filtered, and then examined by the copper test. Should the liquid under examination be free, or nearly so, from organic matter, some of the other tests for the acid may be applied.

When these examinations show the presence of nitric acid, it may become necessary to prove that it was not in the form of a nitrate and the acidity of the solution due to the presence of some other acid. For this purpose a portion of the solution is evaporated to dryness, when if it leave no saline residue it follows that the acid existed in its free state. If, however, it leave a saline residue, the examination must be conducted on the same principles as pointed out for the determination of sulphuric acid under like circumstances (*ante*, 115).

Should the suspected solution be mixed with solid organic matters, the mixture, after the addition of pure water if necessary, is gently boiled for about twenty minutes, allowed to cool, filtered, the solids on the filter washed, and the concentrated filtrate tested. In thus preparing an organic mixture containing free nitric acid, it is well to bear in mind that a portion of the acid may undergo decomposition: for this reason it is sometimes best to neutralize the acid by an alkali before subjecting the mixture to the action of heat. When the prepared liquid contains even only a limited quantity of organic matter, the copper test is the only one that can be reliably applied.

Nitric acid may be separated and purified from organic matters by neutralizing the solution, if this has not already been done, with pure carbonate of potassium or of sodium, whereby the acid will be converted into potassium or sodium nitrate, as the case may be; the liquid is then, after filtration if necessary, concentrated at a moderate heat until a small portion removed to a watch-glass deposits crystals on cooling, when the mass of liquid is allowed to stand in a cool place until the crystals have separated. If the crystals consist of potassium nitrate, they will usually be in the form of long striated six-sided prisms; if of the nitrate of sodium, they usually appear in the form of small obtuse rhombohedra. As both of these salts are freely soluble in water, much of the salt may fail to separate from

the liquid. The crystals are now removed from the liquid, drained and dried. By again concentrating the decanted liquid, a second crop of crystals may be obtained. If the crystals be highly colored, as will usually be the case when obtained from very complex organic mixtures, they are coarsely powdered and washed with absolute alcohol, which will remove much of the foreign matter without dissolving more than a mere trace of the salt. They are then dissolved, by the aid of a gentle heat, in a small quantity of pure water, and again separated by recrystallization, when they will generally be sufficiently pure for the application of any of the tests. A small crystal may now be examined by the brucine test, and the result confirmed by some of the other tests, especially the copper method. Although the copper reaction is the least delicate of the several tests for nitric acid, yet for medico-legal purposes its results are the most satisfactory.

Contents of the Stomach.—These are carefully collected, their reaction noted, and then gently boiled for some time with a proper proportion of water, the solution filtered, and the concentrated filtrate examined in the manner above described. Should an alkaline carbonate or a carbonate of lime or magnesia have been administered as an antidote, the whole of the acid may be in the form of a nitrate of one of these bases, and the mixture have a neutral reaction. In case the potash or soda antidote was employed, the examination is conducted as before for the separation of the alkaline nitrate; but when the lime or magnesia antidote was administered, the concentrated filtered solution is treated with potassium or sodium carbonate as long as it produces a precipitate, whereby the base of the earthy nitrate will be converted into an insoluble carbonate, while the acid will be changed into an alkaline nitrate. This mixture is then heated for some minutes to cause the complete subsidence of the insoluble carbonate, and the solution filtered, after which the filtrate is concentrated and the nitrate separated in its crystalline state.

From organic fabrics.—Stains produced by this acid on articles of clothing and like substances have usually at first a more or less yellow color, then become reddish, and after a time yellowish-brown. The presence of the acid may be determined by boiling the stained portion of the article in a very small quantity of pure water, filtering, and concentrating the filtrate, when, if even only a minute quantity of the acid is present, the liquid will have an acid reaction. The solution is then tested in the usual manner. Instead of boiling

the stained substance with pure water, it may be boiled with a very dilute solution of potassium or sodium carbonate, the acid being thus at once converted into the form of a nitrate. As nitric acid is volatile and more readily decomposed than sulphuric acid, it much more readily disappears from stained articles of clothing. Nevertheless, Dr. Christison detected it in stains on cloth after the lapse of seven weeks; and Dr. Guy quotes an instance in which it was recovered under similar circumstances after an interval of some months.

The yellow stains produced by nitric acid on the skin after a time assume a brownish-yellow color. When these spots are moistened with a solution of caustic potash, they immediately acquire a bright orange hue, wherein they differ from somewhat similar stains occasioned by iodine and bromine, which, at least when recent, on the application of the alkali immediately disappear.

Quantitative Analysis.—There is no ready method of estimating the amount of nitric acid when in solution with other substances. If the liquid be simply a diluted solution of the acid, the quantity of the latter may be estimated sufficiently near for most purposes from the specific gravity of the fluid. When the acid exists in its free state and the solution contains no other acid (except sulphuric), its exact quantity may be determined as follows. The solution is treated with very slight excess of baryta water, and slowly evaporated to dryness: during the evaporation the excess of baryta added will absorb carbonic acid from the atmosphere and become changed into barium carbonate, which is insoluble in water. The dry residue is then treated with a sufficient quantity of pure water, and the solution filtered. The filtrate, which now contains the whole of the nitric acid in the form of barium nitrate, is treated with diluted sulphuric acid as long as a precipitate is produced; the sulphate of barium thus thrown down is collected on a filter, washed, dried, and weighed. Every one hundred parts by weight of sulphate of barium thus obtained correspond to 54 parts of monohydrated nitric acid, or 77.2 parts of acid of specific gravity 1.424, every 81 grains of the latter of which measure about one fluid-drachm.

If during the investigation the acid has been converted into potassium nitrate, this is transformed into the sulphate by treating

the concentrated solution with sufficient sulphuric acid. The mixture is then cautiously evaporated to dryness, and the residue heated to dull redness, when the nitric acid will be entirely expelled and leave for each equivalent one equivalent of neutral sulphate of potassium. If the residue on cooling be not entirely neutral in its reaction, it is moistened with a little acid carbonate of ammonium solution and again heated. Every one hundred parts by weight of this salt correspond to 72.4 parts of monohydrated nitric acid.

Section III.—Hydrochloric Acid.

Hydrochloric or *muriatic acid*, formerly called *spirit of salt*, as found in commerce, is a more or less yellow, powerfully acid liquid, which evolves irritating fumes when exposed to the air. But few cases of poisoning by this substance are reported, and, among these, only perhaps in two instances was it criminally administered. In its action upon the tissues it is somewhat less corrosive than either of the acids already considered.

Symptoms.—The symptoms produced by hydrochloric acid are very similar to those observed in poisoning by sulphuric acid. When the acid is swallowed in its concentrated state, the patient immediately experiences an intense burning sensation throughout the parts with which the liquid comes in contact, attended with a sense of suffocation and the eructation of gaseous matters. These effects are usually sooner or later succeeded by violent vomiting, great restlessness, intense pain in the stomach, coldness of the extremities, and a small, frequent pulse. At first the tongue and throat usually present a white appearance; in a few instances, white fumes were observed to escape from the mouth soon after the poison had been taken. In some instances, on account of the great soreness of the throat and swollen condition of the neighboring parts, there is great difficulty of swallowing. The bowels usually become obstinately constipated, and the urine scanty or entirely suppressed.

Dr. Ogle briefly relates the following case (*St. George's Hosp. Rep.*, iii. 239). A man, aged twenty-five, swallowed two ounces of hydrochloric acid, and when seen two hours later, he having vomited some dark-green matter which effervesced on the addition of sodium carbonate, his skin was warm, pulse 58, and small; the tongue was dry and excoriated. Later on, he complained of great soreness of the throat and fauces, with pain at the epigastrium, and difficulty of

swallowing. In spite of treatment, the patient sank, and died on the ninth day.

In a case cited by Orfila (*Toxicologie*, 1852, i. 195), in which a man had administered to him by mistake about one ounce and a half of hydrochloric acid, there was extreme agitation, with a hot and dry skin, small and hard pulse, fiery-red tongue, blackness of the lips, hiccough, repeated efforts to vomit, and intense pain in the stomach. These symptoms were followed by vomiting of yellow matters, cold and clammy skin, increased pain, extremely frequent pulse, and continuous delirium, and death within about twenty hours after the poison had been taken.

In a singular case quoted by Dr. Christison (*On Poisons*, 148), a man, with suicidal intent, swallowed a quantity of the acid, and exhibited no signs of uneasiness for some time afterward; he then, however, suddenly became faint and fell down. In about three hours after the acid had been taken magnesia and milk were administered, but without relief. He suffered intense thirst, complained of excessive pain in the throat and stomach, and died in about fifteen hours.

If the patient quickly swallows the acid, it may have little or no action upon the tissues of the mouth. Thus, in a case recently reported by Dr. MacDonald, in which a man had swallowed an ounce and a half of hydrochloric acid, there was found no corrosion of the mucous membrane either of the mouth or fauces. (*Edin. Med. Jour.*, June, 1881, 1093.) Under the prompt administration of antidotes the patient in this case soon entirely recovered.

Period when Fatal.—Most of the recorded cases of poisoning by hydrochloric acid were followed by death. The most rapidly fatal case yet recorded is, perhaps, that mentioned by Dr. Christison, in which two ounces of an equal mixture of strong hydrochloric acid and tincture of steel (muriated tincture of iron?) caused death in *five hours and a half*. Vomiting occurred soon after the mixture was taken, but subsequently ceased. Although the patient retained her consciousness until the time of death, she made no complaint either of heat or pain anywhere, or of thirst; but the pulse was imperceptible, and the muscles of the extremities contracted. In three other instances, two of which have already been cited, death took place in fifteen, eighteen, and about twenty hours, respectively. But a case has already been mentioned in which a dose of two ounces did not prove fatal until after a period of *eight days*. And two in-

stances are recorded in which death did not occur until *eight weeks* had elapsed. (Orfila, *Toxicol.*, i. 221; and *Taylor on Poisons*, 291.)

Fatal Quantity.—In a case reported by Dr. Budd, *half a fluid-ounce* of the acid, taken with suicidal intent, proved fatal in eighteen hours to a woman aged sixty-three years. (*Lancet*, July, 1859, 59.) This seems to be the smallest fatal dose yet recorded. In this case the following symptoms were observed: vomiting, collapse, whitening and abrasion of the lips, mouth, and fauces; also, swelling of the throat and inability to swallow, with stridulous breathing and thick inarticulate voice, and intense epigastric pain. Death, without loss of consciousness until near the last, took place by exhaustion.

On the other hand, Dr. Toothaker reports a case in which a man recovered after having taken, by mistake, one ounce of officinal muriatic acid. It was immediately succeeded by violent burning of the mouth and fauces, a sense of suffocation, and spasms. After the administration of olive oil, followed by a mixture of milk and calcined magnesia, copious vomiting ensued. The strength of the patient became greatly reduced, and the extremities so cold as to require the application of sinapisms. The next day there was pain and costiveness, but these were relieved by a dose of castor oil. After this, the patient very gradually recovered. (*Boston Med. and Surg. Jour.*, xv. 270.)

The following case of recovery is reported by Dr. Stevenson (*Guy's Hosp. Rep.*, xiv. 270). A man drank half a wineglassful of strong hydrochloric acid, supposing it to be brandy. When taken to the hospital very soon after, the patient was almost asphyxiated, foamed at the mouth, and breathed with great difficulty. The mouth and fauces were clogged with tough, viscid mucus, and the tongue and adjacent parts appeared excoriated. His speech was thick and indistinct; he complained of great dryness of the mouth and fauces, and of a severe burning pain in the throat, more particularly in the stomach. Vomiting had occurred several times on his way to the hospital. Olive oil was administered, and then several raw eggs, the latter with much relief. The next day only slight signs of the local action of the acid were visible about the mouth and lips; but he experienced great thirst, with a burning pain in the throat. Six days after taking the acid the pain in the throat had much diminished, and the next day the patient was discharged nearly well. In another case recovery took place after about a quarter of an ordinary tumbler-

ful of the commercial acid had been taken at a draught by a woman. In this instance the lips, mouth, and tongue were deprived of their epithelium, red, and inflamed; the fauces and throat were much swollen, and upon the velum and pharynx there was an exudation closely resembling the false membrane of diphtheria.

TREATMENT.—The proper chemical antidote is either chalk or calcined magnesia, or a dilute solution of an alkaline carbonate. If neither of these substances be at hand, milk, white of egg, oil, or demulcents of any kind should be freely administered. In every respect the treatment is the same as in sulphuric acid poisoning (*ante*, 101).

POST-MORTEM APPEARANCES.—In acute cases, the mucous membrane of the mouth, throat, and œsophagus is usually more or less softened, and of a whitish or brownish color. The lining membrane of the stomach is generally highly inflamed, softened, and readily separated. In the case cited above which proved fatal in five hours and a half, the lower portion of the œsophagus had the appearance of being charred. The mucous membrane of the stomach presented black elevated ridges, as if charred, while the intervening furrows were of a scarlet-red color; similar appearances were observed in the duodenum and jejunum. In Dr. Budd's case, the mucous membrane of the mouth, fauces, and larynx was whitened and softened, the soft palate and tonsils were swollen, and a portion of the lining membrane of the larynx was entirely removed. In this case, the local action of the poison was chiefly confined to the parts just mentioned.

In the case cited by Orfila which did not prove fatal until after a period of eight weeks, the lining membrane of the throat and œsophagus was thickened and in a state of suppuration. The stomach was entirely disorganized, softened, and presented several round perforations having thickened and inflamed edges; the pyloric orifice was thickened and contracted. In the small intestines, the mucous membrane throughout its extent was thickened, injected in patches, and of an arborescent appearance; the large intestines were healthy, and contained a brownish, fetid liquid.

CHEMICAL PROPERTIES.

GENERAL CHEMICAL NATURE.—*Anhydrous* hydrochloric acid is a gaseous compound of hydrogen and chlorine, HCl. It is a

colorless, powerfully suffocating gas, having a density of 1.26; when it comes in contact with the air it produces white fumes, due to its strong affinity for water.

Hydrochloric acid, or muriatic acid of the shops, is an aqueous solution of the gaseous compound, of which, according to Davy, water at a temperature of 4.5° C. (40° F.) will absorb 480 times its volume, increasing both in volume and in density. Such a solution has a specific gravity of 1.21, and contains nearly 43 per cent. of anhydrous acid. The solution is colorless, has a highly irritating odor, and yields dense white fumes when a rod moistened with ammonia is presented to it. If the solution be heated, a portion of the anhydrous acid is readily expelled in the form of vapor.

The following table, according to E. Davy, exhibits the percentage by weight of the anhydrous acid in pure aqueous solutions of different specific gravities:

STRENGTH OF AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID.

Sp. Gr.	Percentage of HCl.	Sp. Gr.	Percentage of HCl.	Sp. Gr.	Percentage of HCl.
1.21	42.43	1.14	28.28	1.07	14.14
1.20	40.80	1.13	26.26	1.06	12.12
1.19	38.38	1.12	24.24	1.05	10.10
1.18	36.36	1.11	22.22	1.04	8.08
1.17	34.34	1.10	20.20	1.03	6.06
1.16	32.32	1.09	18.18	1.02	4.04
1.15	30.30	1.08	16.16	1.01	2.02

Hydrochloric acid as found in the shops has usually a density of about 1.15, and a more or less yellow color, due to the presence of free chlorine gas or chloride of iron, or both. It is also liable to be contaminated with sulphuric and sulphurous acids, arsenic, nitric acid, and some of the lower oxides of nitrogen, lead, and common salt; occasionally other impurities are present.

Liquid hydrochloric acid is readily decomposed by iron, zinc, and the stronger electro-positive metals, with the formation of a chloride of the metal and the evolution of hydrogen gas. But it is unacted upon by metallic copper, even at the boiling temperature: in this respect it differs from nitric and sulphuric acids. It is readily decomposed by the basic metallic oxides and their carbonates, with

the formation of a chloride and water, and, in the case of a carbonate, the evolution of carbonic acid.

The *salts* resulting from this acid, or *chlorides* as they are termed, are mostly colorless, and, with the exception of the chlorides of silver and lead and mercurous chloride, are freely soluble in water. When heated with diluted sulphuric acid, the soluble chlorides, together with water, are readily decomposed, giving rise to a sulphate and evolving hydrochloric acid gas; thus: $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$.

Special Chemical Properties.—When hydrochloric acid is heated with black oxide of manganese, both compounds undergo decomposition with the formation of the chloride of the metal and the evolution of free chlorine; thus: $MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2$. The presence of the eliminated chlorine may be recognized by its peculiar odor, its bleaching properties, and, if not in too minute quantity, its greenish-yellow color. Its bleaching property is readily determined by exposing to it a slip of moistened litmus-paper, or a slip of paper moistened with a solution of indigo; if a slip of starch-paper be moistened with a solution of iodide of potassium and exposed to the gas, it immediately acquires an intense blue color, which after a time, under the continued action of the gas, is partially or wholly discharged. If the evolved gas be brought in contact with a drop of a solution of nitrate of silver, or be conducted into a solution of this salt, it produces in the first instance a white film, and in the second a white precipitate, of chloride of silver, having the properties to be presently described.

When a soluble *chloride* is mixed with black oxide of manganese and heated with sulphuric acid, previously diluted with about an equal volume of water, the whole of the chlorine is eliminated in its free state. The reactions in this case, taking chloride of sodium as the type, are as follows: $2NaCl + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2$. The presence of the evolved chlorine may be determined by the methods just indicated. If this decomposition be conducted in a thin watch-glass covered by an inverted glass containing slips of the moistened test-papers, the fractional part of a grain of the salt will yield satisfactory results.

Since the compounds resulting from hydrochloric acid are, with very few exceptions, freely soluble in water, there are but few reagents that precipitate it from solution. In the following investiga-

tions in regard to the behavior of solutions of hydrochloric acid, pure aqueous solutions of the free acid were chiefly employed. The fractions indicate the amount of the anhydrous acid in solution in one grain of liquid, and the results, the behavior of *one grain* of the solution.

1. *Silver Nitrate.*

Nitrate of silver throws down from solutions of hydrochloric acid, of chlorides, and of free chlorine a white amorphous precipitate of chloride of silver, AgCl, which is readily soluble in ammonia, but insoluble in nitric and sulphuric acids; it is also readily soluble in cyanide of potassium, but insoluble in the fixed caustic alkalies. When exposed to light, chloride of silver soon acquires a purple color; on the application of heat, it readily fuses, without decomposition, to a yellowish liquid, which on cooling solidifies to a hard, compact, nearly colorless mass.

1. $\frac{1}{100}$ grain of anhydrous hydrochloric acid, in one grain of water, yields a very copious, curdy precipitate.
2. $\frac{1}{1000}$ grain: much the same results as 1.
3. $\frac{1}{10,000}$ grain yields a very good flocculent precipitate. The solution strongly reddens litmus-paper.
4. $\frac{1}{50,000}$ grain: a very satisfactory deposit. The solution, after a time, slightly reddens litmus-paper.
5. $\frac{1}{100,000}$ grain: in a few moments, a distinct cloudiness, which soon becomes well marked.
6. $\frac{1}{500,000}$ grain yields, after a little time, a slight opalescence.

Nitrate of silver also produces in solutions of *hydrocyanic acid,* even when strongly acidulated, a white precipitate of cyanide of silver, which, like the corresponding chlorine compound, is soluble in ammonia (although less freely), and insoluble in nitric acid. But the cyanide of silver, when dried and heated in a reduction-tube, readily undergoes decomposition, with the evolution of an inflammable gas, in which respects it differs from the chlorine salt. A more ready method of distinguishing between these acids is to treat a portion of the suspected solution with the mercury reagent described below.

In *neutral* solutions, nitrate of silver produces precipitates with several other acids or elements. All of these precipitates, however, except that from hydrocyanic acid, unlike the chloride of silver, are readily soluble in nitric acid, at least in its concentrated state. So,

again, the reagent is readily decomposed, with the production of a white precipitate, by a great variety of organic substances; these precipitates, however, like those just mentioned, are soluble in nitric acid.

The chlorine may be recovered in a soluble form from the chloride of silver, by fusing the latter with a mixture of sodium and potassium carbonates, when the chlorine will be transformed into an alkaline chloride, readily soluble in water.

2. *Mercurous Nitrate.*

This reagent produces in solutions of free hydrochloric acid and of chlorides a white amorphous precipitate of mercurous chloride, or calomel, Hg_2Cl_2, which is insoluble in concentrated nitric acid. The precipitate is readily decomposed by the caustic alkalies, with the formation of a black compound of mercury.

1. $\frac{1}{100}$ grain of the anhydrous acid yields a very copious precipitate.
2. $\frac{1}{1000}$ grain yields much the same results as 1.
3. $\frac{1}{10,000}$ grain: a quite good precipitate.
4. $\frac{1}{50,000}$ grain: a very satisfactory deposit.
5. $\frac{1}{100,000}$ grain yields, after a little time, a very distinct turbidity.

Mercurous nitrate also produces white precipitates in solutions of several other substances. When the reagent is added to a solution of free hydrocyanic acid, as well as of a cyanide, one-half of the mercury is thrown down in its finely divided state as a dark-gray precipitate, while the other portion remains in solution in the form of cyanide of mercury. This reaction, as intimated above, readily serves to distinguish between hydrochloric and hydrocyanic acids, as well as between their salts.

3. *Lead Acetate.*

Acetate of lead produces in solutions of hydrochloric acid and of its salts, when not too dilute, a white precipitate of chloride of lead, $PbCl_2$, which is somewhat less soluble in diluted nitric acid than in pure water. The precipitate is rather freely soluble in boiling water, from which on cooling it separates in its crystalline state.

1. $\frac{1}{100}$ grain of hydrochloric acid, when treated with the reagent, crystals immediately begin to separate, and in a little time there is a quite good crystalline deposit, Plate III., fig. 1.
2. $\frac{1}{200}$ grain: on agitating the mixture with a glass rod, it yields,

after a few minutes, some few crystals of chloride of lead, which are chiefly confined to the margin of the drop.

Acetate of lead also produces white precipitate—usually, however, amorphous—in solutions of several other acids, especially if the mixture be neutral. Moreover, the reagent is readily decomposed by various organic substances, with the production of a white amorphous precipitate.

Separation from Organic Mixtures.

Suspected Solutions.—If the solution has a strong acid reaction, and is tolerably free from organic matter, a small portion of the liquid may be treated with a few drops of a strong solution of nitrate of silver. If this produces a white precipitate, which when washed in diluted nitric acid is insoluble in the stronger acid, there is little doubt of the presence of chlorine. If this examination indicates the presence of chlorine, it then becomes necessary, even should the solution have a strong acid reaction, to determine whether it existed in the form of free hydrochloric acid or as a chloride. For this purpose, a portion of the solution is evaporated to dryness and gently ignited, when if it leaves no saline residue it is quite certain that the acid was uncombined. Should, however, it leave such a residue, this is dissolved in water and tested for chlorine. If this element be absent, it is most probable that the acid was free: however, a mixture of a chloride, as common salt, and excess of sulphuric acid would, as heretofore pointed out in the consideration of the recovery of sulphuric acid, yield upon evaporation a residue entirely free from chlorine. Whether these conditions really existed could be readily determined by treating a portion of the suspected solution with chloride of barium, when if it failed to yield a precipitate, or gave one readily soluble in nitric acid, the absence of sulphuric acid would be fully established.

Should the suspected liquid on evaporation leave a residue containing a chloride, it then becomes necessary to ascertain whether the whole of the hydrochloric acid may have existed in that form. To effect this, a given portion of the liquid is neutralized by pure sodium carbonate, evaporated to dryness, the incinerated residue dissolved in water containing a little nitric acid, the chlorine precipitated by nitrate of silver, and the precipitate collected, washed, dried, and weighed: an equal volume of the liquid, without the addition of carbonate of

sodium, is then evaporated to dryness, the residue incinerated, and the chlorine precipitated, as in the previous operation, by nitrate of silver. If the weight of the precipitate obtained by the former of these methods exceed the weight of that obtained by the latter, then a portion of the acid existed in its free state: the exact quantity of the acid thus present may, of course, be readily deduced from the difference thus observed.

For the separation of free hydrochloric acid from complex mixtures containing organic solids, it has been proposed to heat the mixture, after the addition of water if necessary, to near the boiling temperature, then filter, and distil the filtrate at a gentle heat to the consistency of a thin syrup, the distillate being collected in a proper receiver. The liquid thus collected is then examined by the silver test. As, however, hydrochloric acid strongly adheres to organic matter, none of the acid, unless present in comparatively large quantity, may pass over into the receiver. Under these circumstances, Orfila recommended to treat the residue in the retort with a solution of tannin, filter, and then distil the filtrate, as before, to near dryness. From what has already been stated, it is obvious that if the mixture thus distilled contained a chloride and free sulphuric acid, it would give rise to hydrochloric acid, which would appear in the distillate. This objection could, of course, be answered by testing a portion of the residue with chloride of barium.

Contents of the Stomach.—Any solids present are cut into small pieces, and the mass, after dilution with distilled water if necessary, kept at near the boiling temperature for half an hour or longer, then strained, the strained liquid filtered, and then submitted to the process of distillation described above. If, however, an alkaline or earthy antidote has been administered, and the mixture has a neutral reaction, then a given portion of the filtered liquid is evaporated to dryness, the incinerated residue dissolved in water, and any chlorine present estimated in the form of chloride of silver. In these investigations it must be borne in mind that the gastric juice contains not only alkaline chlorides, but also, it is said, free hydrochloric acid; and, moreover, that common salt, or chloride of sodium, is almost universally present, at least in minute quantity, in articles of food. The gastric juice, however, according to most observers, normally contains only the merest trace of the free acid; but the chlorides exist in very notable quantity.

From the facts just stated, it is obvious that the detection of a mere trace of free hydrochloric acid, or of a chloride in minute quantity, would not in itself be any evidence of poisoning by this acid. If it be shown that the base of the chloride present corresponds to that of the antidote alleged to have been administered, this fact may materially assist in forming an opinion as to the true nature of the case. When the whole of the acid has been converted into a chloride by the administration of an antidote, it may be recovered in its free state by first evaporating the mixture to dryness, then distilling the incinerated residue with strong sulphuric acid, and collecting the evolved acid in a small quantity of water contained in a well-cooled receiver.

For the detection of *free* hydrochloric acid in the contents of the stomach, L. Bouis advises (*Ann. d'Hyg.*, 1874, i. 457) to add a small quantity of binoxide of manganese, and gently heat the mixture, when any hydrochloric acid present, but not common salt or a chloride, will evolve free chlorine, which may be recognized by its bluing action upon paper moistened with a solution of potassium iodide and starch paste. Or, the suspected contents may be heated with a little nitre, when any free hydrochloric acid present will give rise to aqua regia, while with common salt or a chloride no such change will take place. The presence of any aqua regia thus formed may be determined by its solvent action upon gold-leaf, and from the amount of gold dissolved the amount of free hydrochloric acid can be calculated. By the latter method, L. Bouis states that he recognized a few centigrammes of hydrochloric acid in the presence of a large quantity of liquid.

From organic fabrics.—Stains produced by hydrochloric acid on articles of clothing, and like substances, may be examined by gently boiling the stained portion with pure water for some minutes, and testing the filtered liquid in regard to its reaction upon litmus-paper, and with a solution of nitrate of silver. When chlorine is thus discovered, it should be determined, in the manner already pointed out, whether it exists in the form of the free acid or simply as a chloride. As hydrochloric acid is volatile, it sooner or later entirely disappears from stains of this kind.

Quantitative Analysis.—The quantity of free hydrochloric acid, or its equivalent in the form of a soluble chloride, is most

readily determined by precipitating it as chloride of silver. The solution is treated with a solution of silver nitrate as long as it yields a precipitate, and the mixture gently heated until the whole of the precipitate has deposited; the precipitate is then collected on a small filter, thoroughly washed, dried, and weighed. Every one hundred parts, by weight, of chloride of silver thus obtained correspond to 25.43 parts of anhydrous hydrochloric acid, or about 81 parts of liquid acid of specific gravity 1.15; one fluid-drachm of the latter acid weighs about sixty-five and a half grains.

CHAPTER III.

OXALIC ACID, HYDROCYANIC ACID, PHOSPHORUS.

Section I.—Oxalic Acid.

History.—Oxalic acid, in its crystalline state, is an organic compound of the elements carbon, hydrogen, and oxygen, combined with water, its composition being $C_2H_2O_4,2H_2O$. It is found in the common rhubarb-plant, wood-sorrel, and several other plants, and is occasionally met with in human urine, only, however, as an abnormal product. For commercial purposes it is usually obtained by the action of nitric acid upon starch or sugar. In its uncombined state it is a white crystalline solid, having an intensely acid taste. From its close resemblance to sulphate of magnesium, or Epsom salt, it has on several occasions been fatally mistaken for that substance. Either alone, or in combination in a soluble form, it is a powerful poison, and has in several instances been administered as such; but it has much more frequently been taken for the purpose of self-destruction.

Symptoms.—The symptoms produced by oxalic acid depend not only on the quantity taken, but also, somewhat, on the degree of concentration under which it exists. When swallowed in large quantity and in a concentrated state, it produces an immediate burning pain in the mouth and throat, succeeded by vomiting and intense pain in the stomach, and, as the case advances, great muscular prostration, with hurried respiration, pale and anxious countenance, cold and clammy skin, small and feeble pulse, and, in some instances, delirium and convulsions. The vomited matters have not unfrequently contained blood.

When the dose is not large or is much diluted, nothing more than a strongly acid taste may be experienced in the mouth and throat, and the pain in the stomach, as well as the vomiting, may be

much delayed. Although early and continuous vomiting is a common symptom, yet it has in some cases been entirely absent. In a case quoted by Dr. Christison, a man swallowed half an ounce of the poison, dissolved in ten parts of water, without experiencing any pain in the abdomen for six hours, and there was no vomiting for seven hours, except when emetics were administered. In most of the instances in which no vomiting occurred, the dose was either small or greatly diluted; but this symptom has been absent when the poison was taken in large quantity and in a concentrated state.

A man, aged twenty-one years, swallowed with suicidal intent about an ounce of the poison. He instantly felt a burning sensation in the mouth, throat, and œsophagus, and intense pain in the stomach. He soon vomited, and when taken to the hospital complained of a burning sensation along the course of the œsophagus and in the stomach; there were lividity of the face and extremities, relaxation of the muscles, and the surface was cold and clammy; the heart's action was irregular, and the sounds somewhat distant; respiration was natural; pulse extremely feeble; tongue large, œdematous, and covered with thick, woolly fur; conjunctivæ dusky; pupils natural. An emetic removed from the stomach a large quantity of green-looking fluid. After a time the patient appeared much better, and continued to improve until the fifth day, when he arose to relieve his bowels, and died almost immediately. (*Lancet*, Nov. 1860, 509.) In another case, a woman, aged twenty years, to destroy herself took a quantity of oxalic acid, and died from its effects within about twenty minutes.

In a protracted case reported by Dr. C. T. Jackson (*Boston Med. and Surg. Jour.*, xxx. 17), the following symptoms were observed. A man, aged thirty years, took in solution about one ounce of crystallized oxalic acid, mistaking it for Epsom salt. He immediately perceived, by the strong acid taste and burning sensation in the throat, that he had made a mistake, and he drank a large quantity of warm water to excite vomiting, which produced the desired effect. He also took, by the advice of a physician, ipecacuanha and antimony in emetic doses, and castor oil. The matter first vomited was of a dark chocolate color. In twelve hours after the occurrence the patient was in a state of complete prostration: face, lips, throat, and tongue swollen and livid; pulse almost extinct, fluttering and irregular; heart in a continual fluttering palpitation; great jactitation and distress; with incessant vomiting. The matter

vomited was a thick, grumous, and jelly-like fluid, of a yellow color, mixed with white flocculi. He complained of no pain at the epigastrium, or over the bowels, on pressure. Carbonate of lime was now administered, but rejected. On the second day the face was tumid, and of a livid color; tongue swollen and livid; pulse 130; and the urine entirely suppressed. The vomiting continued for two or three days, with great distress and anxiety; the tongue became covered with a brown coating, the tip of the organ being red and dry; and there was great thirst, but no pain. On the sixth day his mind began to wander, and petechiæ appeared on the face, chest, and other parts of the body, which appeared as if sprinkled with blood. He continued to fail, and died on the tenth day after the poison had been taken. In several of the reported cases there was great irritability of the bowels, with frequent purging, and the discharged matters in some instances contained blood.

Oxalic acid is equally poisonous in the form of an alkaline oxalate as when taken in its free state. A woman swallowed some of the acid oxalate of potassium. In two or three minutes she threw up her arms and fell down insensible. In half an hour an emetic was given, but without inducing vomiting. Half an hour later she had partially recovered consciousness. The mucous membrane of the mouth and pharynx was injected, and the tonsils were enlarged, but there was no loss of membrane. Chalk mixture was administered, and afterward vomiting was induced. The next day she complained of slight tenderness of the abdomen, and soreness of the throat and mouth, and there were some slight excoriations on the inner side of the lips. Two days later the patient was discharged as convalescent. (*Guy's Hosp. Rep.*, 1874, 416.)

Period when fatal.—Much the larger proportion of the recorded cases of poisoning by oxalic acid proved fatal; and among these, death in most instances, perhaps, occurred in less than an hour after the poison had been taken. In a case quoted by Dr. Taylor, an unknown quantity of the poison caused death in about *three minutes.* (*On Poisons*, 312.) Dr. Christison refers to two cases which proved fatal in about *ten minutes;* and in another, death ensued in from fifteen to twenty minutes. In a case mentioned by Dr. Pereira, death occurred in twenty minutes. Death also occurred within a similar period in an instance in which the patient vomited almost immediately after the poison had been taken. In an instance in

which the taking of three-quarters of an ounce of oxalic acid was quickly followed by vomiting, and death in about ten minutes, only two grains of the poison were found in the stomach after death.

The fatal period has, however, been delayed for many hours, and even days. Two instances are reported in which death did not occur until thirteen hours had elapsed; and another, in which it was delayed until the fifth day. In Dr. Jackson's case, already mentioned, life was prolonged until the tenth day. The most protracted case yet recorded is, perhaps, that mentioned by Dr. Beck (*Med. Jur.*, ii. 499), in which a woman died from the secondary effects of the poison after a period of some months.

Fatal Quantity.—The effects of given quantities of oxalic acid, like those of most other poisons, have been far from uniform. In one of the cases just referred to, that proved fatal in thirteen hours, *half an ounce* of the poison, largely diluted with water, had been taken. Dr. Taylor quotes a case in which a boy, aged sixteen years, ate about *one drachm* of the solid acid, and it proved fatal within nine hours; and another, in which a woman, aged twenty-eight years, swallowed *three drachms* of the crystallized acid, and was found dead in one hour afterward. These are the smallest fatal doses yet reported. Serious symptoms, however, have followed the taking of much smaller quantities of the poison. In a case reported by Dr. Babington, two scruples of the acid, taken in combination with carbonate of sodium, caused severe symptoms, from which the patient did not entirely recover until some weeks afterward.

On the other hand, complete recovery has taken place after very large quantities of oxalic acid had been taken. Not less than six instances of this kind are reported, in each of which half an ounce of the acid had been swallowed: in most of these, however, early treatment was employed. A like result has also been observed in several instances in which an ounce of the poison had been taken. In a singular case quoted by Wharton and Stillé (*Med. Jur.*, 496), a woman dissolved two large tablespoonfuls of oxalic acid, by mistake for Epsom salt, in a small quantity of water, and took it on an empty stomach. Some twenty minutes afterward she vomited, at first the solution she had taken, and then a dark-colored, bloody fluid, in which were numerous white flakes. Ipecacuanha and afterward prepared chalk were administered, and in about an hour she was found quiet and nearly free from the intense burning pain in her stomach and

throat. She subsequently vomited again, and matters similar to those vomited were discharged from the bowels by purging. Soon after this she entirely recovered. If this case is correctly reported, the quantity of the poison taken was about one ounce and a quarter.

Treatment.—Powdered chalk, magnesia, or its carbonate, suspended in water or milk, or a solution of the acid carbonate of magnesium, should be administered as speedily as possible. Either of these substances will completely neutralize oxalic acid, with the production of an insoluble compound. After thus neutralizing the poison, if there is not free vomiting, an emetic should be administered. Large draughts of warm water may be given to aid the vomiting. One or other of these chemical antidotes has in several instances been employed with great advantage. When, however, the symptoms have once fully manifested themselves, they usually terminate fatally in spite of any treatment.

If neither of these earthy compounds is at hand, an emetic should be given, and its exhibition followed by large quantities of tepid water. The stomach-pump may sometimes be employed with advantage. As the alkaline carbonates form with the acid soluble poisonous salts, they will not serve as antidotes in this kind of poisoning.

Post-mortem Appearances.—These are subject to considerable variation. In rapidly fatal cases, the mucous membrane of the mouth and throat is generally more or less disorganized, and of a white appearance. The lining membrane of the œsophagus is sometimes much softened, and easily detached, and the blood-vessels congested with dark blood. The stomach has been found much contracted in size, and its external coat highly inflamed. The contents of this organ are usually thick, highly acid, and of a dark color, due to the presence of altered blood. The mucous membrane is pale or of a brownish color, injected, softened, and sometimes corrugated. In a few instances the coats of the stomach presented a dark or nearly black appearance; and they have been so much softened as to be lacerated by the slightest pressure. In a case mentioned by Dr. Christison, the coats of the stomach were perforated. The small intestines have in several instances shown signs of irritation; and the liver and spleen have been found in a highly congested state. In this connection, it is important to bear in mind that oxalic acid, even when taken in large quantity, has in some few instances destroyed life without leaving any well-marked morbid

changes, or in fact any abnormal appearance whatever, in the dead body. In a case suddenly fatal on the fourth day after a quantity of oxalic acid had been taken, the walls of the stomach were found somewhat congested, and the organ contained a quantity of bloody fluid; otherwise it was natural.

In a case in which an ounce of oxalic acid had been taken by a man, on an empty stomach, and proved fatal under continued vomiting and purging in *twenty-five minutes*, on inspection the brain, heart, lungs, and kidneys were found healthy. The mucous membrane of the stomach was found highly congested, and curiously *corrugated*, as if the muscular coat had been irritated and contracted. No ulceration or softening was observed. (*Lancet*, Dec. 1860, 593.)

In a case which proved fatal in thirteen hours, the lining membrane of the throat and œsophagus presented an appearance similar to that of having been scalded, and could be easily separated. The stomach contained a pint of thick, dark-colored fluid; and its mucous coat was pulpy, in many points black, and in others highly inflamed; its outer coat was also inflamed. Similar appearances, but in a less degree, were observed both externally and internally in the small intestines. The lining membrane of the trachea was also very red.

In the protracted case reported by Dr. Jackson, the stomach contained a yellow fluid, and was remarkably corrugated; its mucous membrane was much thickened, soft, of a bright red color, and contained numerous small ulcers. The lining membrane of the duodenum was also thickened, red, and studded with ulcers; and that of the other portions of the small intestines congested. The large intestines, and other abdominal organs, were healthy. The heart was empty, except a small quantity of blood in the right side. In a case that proved fatal on the twenty-third day, the lining membrane of the œsophagus and stomach was completely destroyed, and in places entirely removed; and the muscular coat, throughout the gullet and stomach, was much thickened, highly injected, and presented a dark appearance.

Chemical Properties.

General Chemical Nature.—Oxalic acid, when pure, forms colorless, transparent, odorless, four-sided crystalline prisms, which contain two molecules of water of crystallization, $C_2H_2O_4,2Aq$. It

is the strongest of the vegetable acids. The crystals are permanent at ordinary temperatures; but when exposed to warm air, they part with their water of crystallization and become opaque.

Oxalic acid is readily soluble in water at ordinary temperatures. The extent to which the acid dissolves in this fluid has been variously stated at from eight to fifteen times its weight of the liquid. And, in fact, either of these extremes will equally express its solubility, unless some exact temperature be specified. As the mean result of three very closely accordant experiments, we have found that when excess of the pure crystallized acid is kept in contact with pure water for five hours at a temperature of 15.5° C. (60° F.), and the solution then filtered, the filtrate contains one part of the acid in 9.5 parts of water. It is more freely soluble in warm water; and boiling water, it is said, will take up its own weight of the acid. Berzelius met with a sample of the crystallized acid which was so strongly impregnated with nitric acid, used in its preparation, that it required only two parts of cold water for solution. The pure acid is also freely soluble in alcohol, but insoluble in ether, and very sparingly soluble in chloroform. When one grain of the pure crystallized acid is dissolved in one hundred grains of water, and the solution violently agitated, for a few moments, with an equal volume of pure chloroform, this liquid extracts one-twentieth of a grain of the acid.

The *oxalates*, or salts of this acid, are usually colorless and crystallizable, and for the most part, except those of the alkalies, insoluble in water. They are all decomposed by heat, the acid being resolved into carbonic acid and carbonic oxide.

Special Chemical Properties.—Oxalic acid, when pure, is entirely dissipated at a temperature of about 177° C. (350° F.). In this respect it differs from the sulphate of magnesium, which it closely resembles in appearance, and which leaves a fixed residue, even at high temperatures. When the acid is heated with strong sulphuric acid, it is resolved, without charring, into carbonic acid and carbonic oxide gases, which escape: tartaric and other organic acids when thus heated are speedily charred. Solutions of the acid have a strongly acid taste and reaction, even when much diluted, and fail to be precipitated by the alkaline carbonates: a solution of Epsom salt has a bitter taste, is neutral in its reaction, and yields a white precipitate when treated with sodium carbonate.

Pure aqueous solutions of oxalic acid, when slowly evaporated to

dryness, leave the acid in the form of long crystalline prisms. When one grain of a 1–100th solution of the acid is allowed to evaporate spontaneously, it leaves a comparatively large mass of crystals; when the solution contains the 1–1000th of its weight of the acid, it yields a quite good deposit, the crystals having the forms represented in Plate III., fig. 2; the 1–10,000th of a grain of the acid, under similar circumstances, yields a very satisfactory deposit of small prisms and crosslets.

In the following details in regard to the behavior of solutions of oxalic acid, the fractions indicate the fractional part of a grain of the pure crystallized acid in solution in one grain of water; and the results refer to the reactions of one grain of the solution.

1. *Silver Nitrate.*

Solutions of free oxalic acid, and of its alkaline salts, yield with nitrate of silver a white amorphous precipitate of oxalate of silver, $Ag_2C_2O_4$, which is slowly soluble in cold nitric acid, but readily soluble in the heated acid; it is also readily soluble in solutions of ammonia, but insoluble in concentrated solutions of acetic, tartaric, and oxalic acids. When the dried precipitate is heated on platinum foil, it is decomposed and dissipated in slightly detonating puffs, being resolved into metallic silver and carbonic acid gas; thus: $Ag_2C_2O_4 = Ag_2 + 2CO_2$.

1. $\frac{1}{100}$ grain of oxalic acid, in one grain of water, yields a very copious precipitate, which, in the mixture, requires about three drops of strong nitric acid for complete solution. When dried and heated, it is dissipated in the manner peculiar to this salt.
2. $\frac{1}{1000}$ grain yields a rather copious precipitate, which, when dried and heated, is rapidly dissipated, but not in distinct puffs.
3. $\frac{1}{10,000}$ grain: a very good deposit.
4. $\frac{1}{50,000}$ grain yields an immediate turbidity, and, in a very short time, a quite satisfactory deposit.
5. $\frac{1}{100,000}$ grain: an immediate opalescence, and, after a little time, a quite distinct deposit.
6. $\frac{1}{500,000}$ grain yields, after some minutes, a distinct cloudiness.

Fallacies.—Nitrate of silver is also readily decomposed, with the production of a white precipitate, by a great variety of organic principles. And it also produces similar precipitates with several other acids, especially from neutral solutions. Thus, it occasions

precipitates in neutral solutions of the carbonates, tartrates, phosphates, borates, citrates, chlorides, and cyanides, and also, in most instances, with the free acids of these salts. All these precipitates, however, except those from the chlorides, cyanides, and their free acids, are *soluble* in acetic acid, in which respect they differ from the oxalate of silver. So, also, the chloride and cyanide of silver—produced by the reagent from solutions of chlorides and cyanides or their free acids—are readily distinguished from the oxalic acid precipitate, in that they are *insoluble* in nitric acid. Moreover, the chloride of silver, when dried and heated, quietly fuses without decomposition; and the cyanide, under similar circumstances, is decomposed with the production of a *fixed* residue and the evolution of an inflammable gas. The precipitates produced from the carbonates, tartrates, phosphates, borates, and citrates, when dried and heated, also, unlike the oxalic acid deposit, leave a fixed residue.

2. *Calcium Sulphate.*

Sulphate of calcium throws down from solutions of free oxalic acid, and of soluble oxalates, a white granular precipitate of oxalate of calcium, $CaC_2O_4,2Aq$, which is readily soluble in nitric and hydrochloric acids, but insoluble, or very nearly so, in acetic and other vegetable acids. As sulphate of calcium is soluble only to a limited extent in water, its solution does not precipitate the whole of the oxalic acid from somewhat concentrated solutions, unless the reagent solution be added in very large quantity. From such solutions the whole of the acid may be readily precipitated, as calcium oxalate, by employing as the reagent a solution of chloride of calcium or any of the other more soluble salts of lime.

1. $\frac{1}{100}$ grain of free oxalic acid yields with a drop of the calcium sulphate solution a very good, granular precipitate. A small drop of *chloride of calcium* solution produces a much more copious deposit, which is in the form of small rectangular and notched plates, somewhat larger than the granules produced by the sulphate of calcium.
2. $\frac{1}{1000}$ grain: an immediate cloudiness, and soon a quite good granular deposit. *Chloride of calcium* produces much the same reactions, but the precipitate consists chiefly of small plates and octahedral crystals, which vary in size from the 1–3000th to the 1–7000th of an inch, Plate III., fig. 3. The precipitate oc-

casioned by the sulphate of calcium is in the form of oval granules, which uniformly measure about the 1–10,000th of an inch in their longest diameter.

3. $\frac{1}{10,000}$ grain: very soon a perceptible cloudiness, and in a little time a quite satisfactory deposit.
4. $\frac{1}{25,000}$ grain yields, after a little time, a quite distinct turbidity.
5. $\frac{1}{50,000}$ grain: after some minutes, a just perceptible opalescence.

Fallacies.—The reaction of this reagent is much less open to fallacy than that of nitrate of silver. From neutral solutions, however, calcium sulphate produces somewhat similar precipitates with the alkaline carbonates, phosphates, and borates; but from the last-mentioned only when the solution is extremely concentrated. Chloride of calcium also occasions white precipitates in solutions of these salts, and, in addition, in strong solutions of the alkaline citrates. But these precipitates are all readily soluble in acetic acid, and may thus be distinguished from the calcium oxalate. In this connection it may be remarked that even concentrated solutions of free tartaric, citric, hydrochloric, and hydrocyanic acids, and of their salts, fail to yield a precipitate with calcium sulphate. When, therefore, this reagent and nitrate of silver produce in a suspected solution white precipitates, which in both instances are insoluble in acetic acid, the results are not then open to any of the objections thus far mentioned under these tests individually.

Sulphate of calcium also produces white precipitates, even in acid solutions of lead, baryta, and strontia, the sulphates of these metals being thrown down. These precipitates, however, unlike the calcium oxalate, are *insoluble* in nitric and hydrochloric acids; they are also insoluble in acetic acid. Chloride of calcium fails to precipitate solutions of barium and strontium; but it causes in strong solutions of salts of lead a white precipitate of chloride of lead, which slowly disappears on the addition of water.

3. *Barium Chloride.*

This reagent occasions in solutions of free oxalic acid, when not too dilute, a white precipitate of oxalate of barium, which is readily soluble in nitric and hydrochloric acids, but soluble with difficulty in oxalic acid, and still less soluble in acetic acid. As the oxalate of barium is soluble in hydrochloric acid, even when highly diluted, the reagent fails to precipitate the whole of the oxalic acid from

strong solutions of the free acid: since the hydrochloric acid set free by the decomposition prevents the further action of the reagent. The precipitate produced from strong solutions of the acid is usually in the form of groups of bold, sharp-pointed crystalline needles. Neutral solutions of the alkaline oxalates yield with the reagent a white amorphous precipitate, which soon becomes crystalline. This reaction is very much more delicate than when the acid exists in its free state.

1. $\frac{1}{100}$ grain of free oxalic acid yields a quite good amorphous precipitate, which soon becomes granular, and in a little time crystalline, forming in most instances bold dumb-bells and needles, Plate III., fig. 4. If nitrate of barium be employed as the reagent, the precipitate is usually in the form of small octahedral crystals.
2. $\frac{1}{1000}$ grain: after a few moments the mixture becomes turbid, and in a little time yields a good deposit of crystalline needles, and granules.
3. $\frac{1}{5000}$ grain: on stirring the mixture with a glass rod, it yields, after some time, a quite distinct deposit of granules and needles, which under the microscope are quite satisfactory.

Fallacies.—Chloride of barium also produces in solutions of free sulphuric acid and of sulphates a white precipitate of sulphate of barium, which, however, differs from the oxalic acid precipitate in regard to its form, and in being insoluble in strong nitric acid. In neutral solutions the reagent also produces white precipitates with the alkaline carbonates and several other salts; but all these deposits, except that from sulphates, are readily soluble in acetic acid.

4. *Strontium Nitrate.*

Nitrate of strontium throws down from solutions of free oxalic acid a white precipitate of oxalate of strontium, which is very sparingly soluble in acetic and oxalic acids, but freely in nitric and hydrochloric acids. When the acid exists in the form of an alkaline oxalate, the delicacy of the reaction of this reagent is much increased.

1. $\frac{1}{100}$ grain of the free acid yields an immediate precipitate, and in a little time there is a very good deposit of octahedral crystals, plates, and small granules, Plate III., fig. 5.
2. $\frac{1}{1000}$ grain: in a little time, granules, prisms, and octahedral crystals.

3. $\frac{1}{5000}$ grain: in a little time, a distinct turbidity, and soon a rather good granular precipitate.
4. $\frac{1}{10,000}$ grain: in a few minutes, a very distinct granular deposit.

The objections to the reactions of this test, and the methods of answering them, are the same as pointed out under the preceding reagent.

5. *Lead Acetate.*

Solutions of free oxalic acid, and of its soluble salts, yield with this reagent a white precipitate of oxalate of lead, which is insoluble in acetic acid, but readily soluble in nitric acid.

1. $\frac{1}{100}$ grain of the free acid yields a very copious precipitate, consisting of a mass of crystalline needles, Plate III., fig. 6.
2. $\frac{1}{1000}$ grain: a copious precipitate, which immediately begins to crystallize.
3. $\frac{1}{5000}$ grain: a good deposit, which soon becomes changed into stellate crystalline groups.
4. $\frac{1}{10,000}$ grain: an immediate turbidity, and soon, stellate crystals.
5. $\frac{1}{20,000}$ grain: very soon the mixture becomes opalescent, and, in a little time, yields a satisfactory granular deposit.
6. $\frac{1}{40,000}$ grain: after some time, the mixture becomes slightly turbid.

Fallacies.—Solutions of sulphuric acid and of sulphates, and strong solutions of hydrochloric acid and of chlorides, also yield, when treated by the reagent, white precipitates, which, however, are *insoluble* in strong nitric acid. The reagent also produces white precipitates in *neutral* solutions of carbonates, phosphates, and several other salts, and also with a great variety of organic substances. These deposits, however, at least for the most part, are readily soluble in acetic acid.

The oxalic acid may be recovered in its free state from the oxalate of lead by suspending the latter in water and passing through the mixture a stream of sulphuretted hydrogen gas, as long as it causes any blackening of the mixture. By this means the oxalate of lead will be entirely decomposed, the metal being precipitated as black sulphide of lead, while the eliminated acid will remain in solution: $PbC_2O_4 + H_2S = PbS + C_2H_2O_4$. On now warming the mixture, to facilitate the deposition of the precipitate and expel the excess of gas added, filtering, and concentrating the filtrate at a moderate temperature, the solution on cooling, if sufficiently concentrated, will deposit the acid in its crystalline form.

The precipitate produced by the reagent from ten grains of a 1–1000th solution of the free acid, when washed and suspended in ten grains of water, then treated with sulphuretted hydrogen, and the solution filtered, will furnish ten grains of liquid, which when examined in separate drops by the preceding reagents will yield results not to be distinguished from those obtained from a 1–1000th solution of the pure acid. In other words, the 1–100th of a grain of the acid, when in solution in ten grains of water, may be precipitated by acetate of lead and the acid recovered in its free state, without any appreciable loss. The presence of organic matter may, however, considerably modify these results.

6. *Copper Sulphate.*

Sulphate of copper produces in solutions of free oxalic acid, when not too dilute, a precipitate of oxalate of copper, having a very light bluish or greenish color, the tint depending on the strength of the solution. The precipitate is insoluble in acetic and oxalic acids, and dissolves to a very limited extent in even large excess of strong nitric acid; it is also insoluble in salts of ammonia, but dissolves readily in the pure alkali.

1. $\frac{1}{100}$ grain yields a very copious flocculent precipitate.
2. $\frac{1}{500}$ grain: after a little time, a granular precipitate, which for the most part floats on the surface of the mixture; the addition of a few drops of strong nitric acid does not cause the granules to disappear.
3. $\frac{1}{1000}$ grain yields, after some time, a slight precipitate, which is dissolved on the addition of a drop of nitric acid.

Fallacies.—Sulphate of copper also produces precipitates in neutral solutions of carbonates and of phosphates, and is also decomposed by certain kinds of organic matter with the production of a precipitate; but all these deposits are distinguished from the oxalate of copper in being readily soluble in nitric and hydrochloric acids. Solutions of free sulphuric, hydrochloric, tartaric, and citric acids, and of their salts, fail to be precipitated by this reagent.

Separation from Organic Mixtures.

Suspected Solutions.—When the solution contains much organic matter, none of the preceding tests should be applied directly to the mixture, since under these conditions they are all liable to produce a

precipitate, even in the absence of oxalic acid. If the solution is strongly acid in its reaction and contains mechanically suspended solids, the mixture, properly diluted with water if necessary, is digested at a moderate heat for fifteen minutes or longer, then filtered, the filtrate concentrated to a small volume, and, if necessary, again filtered.

As a preliminary step, a drop of the liquid may now be examined by the sulphate of copper test. If this produces a faintly bluish precipitate, insoluble, or nearly so, in nitric or hydrochloric acid, there is little doubt of the presence of oxalic acid. If the precipitate thus produced is quite copious, and the liquid under examination nearly colorless, then the remaining portion, after further concentration if thought best, is allowed to stand in a cool place for some hours, in order that the acid, in part at least, may crystallize out. Any crystals thus obtained are separated from the liquid, gently washed, then dissolved in a small quantity of pure water, and the solution tested in the ordinary manner. On further concentrating the liquid from which the crystals separated, a second crop may be obtained. If the crystals deposited in these operations are highly colored, they should be redissolved in a little warm water and purified by recrystallization before being tested.

Should, however, the preliminary examination by the copper test indicate the presence of only a minute quantity of the acid, or should the liquid be highly colored, then the remaining portion is treated with slight excess of a solution of acetate of lead, by which the whole of the acid will be precipitated as oxalate of lead, together with more or less organic matter. The precipitate thus produced is collected on a filter and thoroughly washed, first with water acidulated with acetic acid, then with pure water. The moist precipitate is then diffused in an appropriate quantity of water and exposed to a stream of sulphuretted hydrogen gas until the whole of the white compound is thoroughly blackened, which may require an hour or longer. By this treatment, as already pointed out, any oxalate of lead present will be decomposed, the acid entering into complete solution, and the metal being thrown down as sulphide. The liquid is now separated from the precipitate by filtration, and kept at a moderate temperature until the odor of the sulphuretted gas has entirely disappeared. It is then, if colorless, examined by the usual tests; if, however, it is highly colored, any oxalic acid

present is purified by crystallization, in the manner above described, and then tested.

The methods now described would yield equal results whether the acid existed in its uncombined state or in the form of a soluble oxalate in the original liquid, and, therefore, do not serve to distinguish the state in which it was present. This, however, in medico-legal investigations, is rarely a matter of much importance. Should it be desired to determine this point, it may be approximatively done by evaporating the prepared filtered liquid to dryness on a water-bath, and extracting the residue with very strong alcohol, which will dissolve the free acid if present as such, together with more or less foreign matter, but only a trace of an alkaline oxalate, nearly the whole of the latter, unless present in only very minute quantity, remaining undissolved. The filtered alcoholic solution may now be evaporated to dryness on a water-bath, the residue digested with a small quantity of water, and the filtered liquid examined by either of the above-mentioned methods. The residue remaining undissolved by the alcohol, supposed to contain an alkaline oxalate, is stirred with distilled water, the solution filtered, and then examined in the usual manner.

Contents of the Stomach.—If no chemical antidote has been administered, the contents of the stomach are collected in a porcelain dish, tested in regard to their reaction, and the inside of the organ well washed with distilled water, the washings being collected with the contents in the dish. The mixture, after the addition of more water if necessary, is heated to about the boiling-point for half an hour or longer, the cooled liquid strained, the solids on the strainer washed, and the united liquids filtered, then concentrated and again filtered. The liquid may now either be evaporated to dryness, and the residue thoroughly extracted by strong alcohol, as described above for suspected solutions, or it may be treated with slight excess of acetate of lead, the precipitate collected on a filter, washed with water acidulated with acetic acid, and any oxalate of lead present subsequently decomposed by sulphuretted hydrogen gas.

Instead of decomposing the oxalate of lead by sulphuretted hydrogen, it has been proposed to boil it for about half an hour in an appropriate quantity of highly diluted sulphuric acid, by which it will be resolved into insoluble sulphate of lead and free oxalic acid. The liquid is then filtered, exactly neutralized by ammonia,

and tested. Under these circumstances, the poison would exist as oxalate of ammonia, mixed with more or less sulphate of ammonium; the latter being formed from the excess of sulphuric acid employed in the decomposition of the oxalate of lead. The presence of this sulphate would not interfere with the reactions of the silver, sulphate of calcium, and copper tests; but it would yield with the barium, strontium, and lead reagents white precipitates of the sulphates of these metals. Of these two methods of effecting the decomposition of the oxalate of lead, the former is much to be preferred.

Should lime or magnesia have been administered as an antidote, the contents of the stomach, as well as any matters vomited prior to death, may have a neutral reaction, and contain the poison in the form of an insoluble oxalate of one or other of these bases. Under these circumstances, the suspected matters, especially all earthy solids, are collected in a dish, the mass made quite liquid by the addition of warm water, and thoroughly stirred; any organic solids present are then washed in the liquid and removed, and the remaining solids allowed completely to subside. When this has taken place, the liquid is decanted, and the solids are again washed with fresh water; they are then diffused in a small quantity of pure water, a quantity of pure potassium carbonate, somewhat exceeding that of the earthy matter present, is added, and the mixture boiled for about half an hour, the liquid evaporated during the operation being replaced by distilled water. The earthy oxalate will now be changed into an insoluble carbonate, while the oxalic acid will be in solution in the form of potassium oxalate. This solution, after filtration, is treated with decided excess of acetic acid, and the oxalic acid precipitated by a solution of acetate of lead. The precipitate thus produced is collected, washed, and decomposed by sulphuretted hydrogen gas in the manner already described.

In case of the discovery of oxalic acid in vomited matters or the contents of the stomach, it might be objected, in a medico-legal investigation, that the acid was a normal constituent of certain vegetable structures, some of which are sometimes used as articles of food or administered medicinally. Thus, it is present in common sorrel, in culinary rhubarb, or pie-plant, and in the rhubarb of the shops. In these substances, however, it exists only in minute quantity, and in its combined state, either as oxalate of potassium or of calcium.

But should even only a minute quantity of the poison be discovered, the symptoms and other circumstances attending a case of poisoning by the acid would rarely leave any doubt whatever as to its true nature.

The Urine.—Oxalic acid, when taken either in its free or combined state into the stomach, soon appears in the urine, usually in the form of octahedral crystals of calcium oxalate. The forms of these crystals readily distinguish them from all other urinary deposits; they are very similar in form to those of the oxalate of strontium, as figured in Plate III., fig. 5. These crystals are often present in the urine at the time it is voided, but more frequently they do not separate until after some hours.

For the purpose of making this examination, a small portion of the liquid is gently rotated in a watch-glass, until the sediment collects at the bottom of the fluid, when the clear liquid is decanted; the sediment is then washed in a similar manner with pure water, which in its turn is decanted, and the deposit examined by the microscope, under an amplification of about one hundred and twenty-five diameters. If none of the crystals are thus found, and the urine is fresh, some ounces of it may be allowed to stand quietly for several hours, the clear liquid decanted, and the sediment collected, washed, and examined as before.

In this connection, it must be borne in mind that these crystals also thus occur not only after the ingestion of certain articles of food, but not unfrequently as the result of disease, and sometimes even without any apparent cause. In fact, we have found the latter to be the case much more frequently than seems to be generally supposed.

If it be desired to examine the urine for the presence of the free acid or of a soluble oxalate, the liquid, after the addition of a little acetic acid, may be evaporated to about one-fourth its volume, filtered if necessary, the filtrate treated with slight excess of acetate of lead, any precipitate thus produced decomposed by sulphuretted hydrogen, and the filtered solution tested by the usual reagents.

Quantitative Analysis.—From pure solutions oxalic acid may be estimated with considerable accuracy in the form of oxalate of lead (PbC_2O_4). The solution is treated with a little pure acetic acid, and a solution of acetate of lead added as long as a precipitate

is produced; when the precipitate has completely subsided, it is collected on a filter of known weight, well washed with pure water, dried at 100° C. (212° F.), and weighed. Every one hundred parts by weight of oxalate of lead thus obtained correspond to 42.5 parts of crystallized oxalic acid.

If the acid has been precipitated as oxalate of calcium, this is thoroughly washed and dried, then exposed for a few minutes to a very dull red heat. In this last operation the oxalate will be converted into calcium carbonate, every one hundred parts of which correspond to one hundred and twenty-six parts of the crystallized acid.

Section II.—Hydrocyanic Acid.

History and Composition.—This substance, also known as prussic acid, is a compound of the organic radical cyanogen (CN) with the element hydrogen, its composition being represented by the formula HCN or HCy. In its pure state, hydrocyanic acid is a colorless, volatile liquid, having a peculiar odor, somewhat resembling that of bitter almonds. It is one of the most powerful and rapidly fatal poisons yet known; and many of its compounds are about equally poisonous. It may be obtained from various vegetable substances, as bitter almonds, the kernels of peaches, plums, apricots, and cherries, apple-pips, the flowers of the peach and cherry-laurel, the bark of wild cherry, and the root of mountain ash. In many of these substances, however, the acid does not exist as such, but is the result of the decomposition to which they are subjected in its preparation.

For ordinary purposes, hydrocyanic acid is usually obtained by distilling one of its salts with dilute sulphuric or hydrochloric acid. The acid of the shops is a solution of the anhydrous acid, usually in water, but sometimes in alcohol, and varies in strength from 1 to 25 per cent., according to the directions of the Pharmacopœia followed for its preparation. The *United States Pharmacopœia* directs a strength of 2 per cent. of the pure acid; and about the same proportion is directed by the British Colleges. The preparation known as Scheele's acid sometimes contains as much as 5 per cent. of real acid, but usually its strength falls very short of this. Of several specimens of commercial acid examined some years since, we found none to contain over 1.5 per cent. of anhydrous acid; and one of the samples, which had not before been opened

after having left the hands of the manufacturer, did not contain even a trace of the acid.

An aqueous solution of hydrocyanic acid, especially when exposed to the light, is prone to undergo spontaneous decomposition, with the formation of a brown deposit. This fact, in a measure at least, accounts for the difference observed in the strength of samples of the acid prepared after the same formula. This decomposition is much retarded by the presence of a minute quantity of a mineral acid, and for that purpose a trace of sulphuric acid is frequently added to the solution. According to J. Williams, aqueous solutions, even when containing 5 per cent. of the acid, may be preserved unchanged for long periods by the addition of 20 per cent. of glycerin. An aqueous solution of the acid, when pure, is perfectly colorless. In regard to its physiological effects, hydrocyanic acid belongs to the class of narcotic poisons.

Symptoms.—These, both in respect to the time within which they appear and their character, depend upon the quantity of the acid taken. When taken in large quantity, it not unfrequently proves so rapidly fatal that no well-marked symptoms are observed. During the act of swallowing a large dose, the patient experiences a hot bitter taste, and is either immediately or at most within a very few minutes seized with complete loss of muscular power and of consciousness. The respiration becomes hurried, but often convulsive, and sometimes stertorous, the pulse imperceptible, the extremities cold, the eyes prominent, the pupils dilated, and in many instances there are convulsions.

In a case reported by Hufeland, in which a man swallowed about forty grains of the pure acid, in the form of an alcoholic solution, the patient immediately staggered a few steps, and then fell, apparently lifeless. When seen, almost instantly afterward, by a physician, the pulse was imperceptible and the respiration entirely suspended. After a short interval, the man made a very forcible expiration; the extremities became cold, the eyes prominent, glistening, and insensible to light, and after a few convulsive expirations he died, within five minutes after the poison had been taken.

The following case was reported to Professor A. Stillé by Mr. Clay Hall. (*Amer. Jour. Med. Sci.*, Jan. 1868, 277.) A gentleman with suicidal intent took about one hundred drops of diluted hydrocyanic acid, purporting to contain 2 per cent. of the anhydrous acid.

When seen by Mr. Hall, within five minutes after taking the poison, the man was found lying extended upon the floor, unconscious. His muscles were relaxed and flaccid, with the exception of the muscles of the jaw, this being firmly closed; his hands were folded across his breast, as in repose; the eyes were fixed, but life-like, the pupils being normal; respiration was slow, but not labored; his pulse was about 50, becoming slower and less strong to the moment of death; the veins of the neck and face were strongly congested. Not the slightest odor of the acid could be perceived in his expirations; nor was any perspiration perceptible. His respiration became slower and slower, until intervals of over one minute intervened, and he quietly died in from fifteen to twenty minutes after taking the poison, the pupils dilating at the moment of death.

It was formerly believed that when prussic acid was taken in rapidly fatal quantity it always produced immediate insensibility; but this is by no means always the case. When taken in such quantity, the symptoms usually appear within a very few seconds, yet they have in several instances been delayed sufficiently long for the patient to perform a series of voluntary acts. In a case related by Dr. Sewell, a man swallowed seven drachms of Scheele's preparation of the acid, believed to contain about twenty-one grains of the anhydrous poison, after which he walked to the door of his room, unlocked it, called for assistance, then walked to a sofa and stretched himself upon it; in a very little time after this he was found in an insensible state, with stertorous breathing, and soon died. (*Boston Med. and Surg. Jour.*, xxxvii. 322.)

The following remarkable case is related by Mr. Hickman. (*Lancet*, 1866, i. 310.) A man, by mistake for some medicine, swallowed half an ounce of the diluted acid, containing, as was afterward determined, something over three grains and a half of the pure acid. After taking the dose, he ran up-stairs to the house-surgeon, traversing a distance of twenty-five or thirty paces, and ascending thirty-two steps. When he reached the surgeon's room he said, "Come down directly; I have taken half an ounce of prussic acid." He then ran all the way back to the dispensary, where he was found standing unsupported in the middle of the room. He moved his hand impatiently, and said, "Be quick; give me something." Some solution of ammonia was given him, followed by some tincture of the sesquichloride of iron. He drank both these,

and then, being directed, put his finger in his throat to induce vomiting. This caused one or two slight but abortive efforts, after which he suddenly fell flat on his back, completely insensible. His face, previously pallid, now became much congested; the eyes were fixed and half closed; the pupils were somewhat dilated; no pulse could be felt; the breathing became slow, faint, and gasping; a frothy mucus exuded from between the lips; one or two of the respirations were accompanied by a slight stertorous sound. No convulsions occurred. Death took place in about ten minutes after he first appeared at the house-surgeon's room.

When the dose is not sufficiently large to produce rapid insensibility, the first symptoms usually experienced are giddiness and a sense of great weakness; these effects are soon succeeded by irritation in the throat, an increased flow of saliva, nausea, difficult and spasmodic respiration, and loss of voluntary motion; the pulse becomes small or imperceptible, the face livid, and the eyes glaring, the pupils generally being dilated. These cases are frequently attended with tetanic convulsions.

The following case of recovery is quoted in detail by Dr. Stillé. (*Mat. Med.*, ii. 210.) A French physician swallowed a dessert-spoonful of the medicinal acid, prepared by a chemist of Paris. He almost immediately afterward fell down as if struck by lightning. Among the symptoms observed were loss of consciousness and sensibility; trismus; a constantly increasing dyspnœa; cold extremities; a noisy and rattling respiration; the characteristic odor of the acid upon the breath; distortion of the mouth; and a thready pulse. The face was swollen and dusky, and the pupils fixed and dilated. The trismus increased, and was soon accompanied by opisthotonos. At the end of an hour a violent convulsion occurred, the whole trunk grew stiff, and the arms were twisted outwards. After two hours passed in this condition, the patient began to regain his consciousness, and in several hours afterward he was able to walk without assistance; but it was a fortnight before he entirely recovered.

In a non-fatal case reported by Mr. W. H. Burnam, in which a dose containing 2.4 *grains* of the anhydrous acid was taken by mistake, insensibility did not occur until *two minutes* after the poison had been swallowed. In the mean time, however, the patient, having almost immediately discovered his mistake, took as an antidote half

an ounce of aromatic spirits of ammonia, with a little water; and he told what had occurred: he spoke hurriedly, and breathed deeply. A solution of sulphate of iron was then administered. The respiration became deeper and slower. In four minutes after the poison was taken, the cold douche was freely employed, and an additional quantity of the iron solution with spirits of ammonia administered. Vomiting took place; and there was a slight convulsive shudder. In twenty minutes the patient began to exhibit signs of returning consciousness; and in about fifteen minutes later he was able to walk up-stairs to bed. (*Brit. and For. Med.-Chir. Rev.*, April, 1854.) In a case of recovery reported by Mr. Garson, in which a teaspoonful of the acid, of unknown strength, had been taken, the symptoms were delayed for about *fifteen minutes*. The individual was then found in a state of insensibility, and this continued for about four hours, although active remedies were employed. This is the most protracted case, in regard to the appearance of the symptoms, yet recorded.

Several instances are reported in which the inhalation of the diluted *vapor* of hydrocyanic acid caused most alarming symptoms; and Dr. Christison quotes a case in which the liquid acid applied to a wound in the hand caused death in an hour afterward. In a case related by Dr. J. A. Post (*New York Med. Jour.*, April, 1876), the inhalation of the vapor evolved from cyanide of potassium used by a jeweller with gold as an alloy caused his death, under symptoms of congestion of the brain, in about half an hour after he was first seen by the physician.

Hydrocyanic acid is also equally poisonous, with the production of similar symptoms, when taken into the system in the form of an alkaline cyanide. Since the introduction of *cyanide of potassium* into the arts for photographic and other purposes, numerous instances of poisoning by it have occurred. In a case of poisoning by this salt related by Dr. Schauenstein, of Vienna, occurring in a young man, death took place almost instantly, without any striking symptoms. In another case, reported by the same writer, strong tetanic spasms came on directly after the poison had been taken, and death ensued in less than an hour. (*Amer. Jour. Med. Sci.*, Jan. 1860, 279.) In a case in which we were consulted in 1864, a man took, with suicidal intent, about sixteen grains of the salt in solution; immediately after swallowing the poison he walked

about six steps, then fell insensible, and death ensued in about five minutes.

The following case of recovery after a quantity of this salt had been taken is reported by Dr. Mueller-Warnek. (*London Med. Record*, May, 1878.) A man was heard to fall in his room, and quickly after was found lying on the floor in an unconscious state, holding in one hand a letter, and in the other a bottle containing a solution of cyanide of potassium. About an hour later, vomiting having occurred, the man was in a state of profound coma. The skin was cold and clammy; the extremities cold; face greatly cyanosed; eyeballs projecting, and directed upwards; pupils much dilated, and insensible to light; the lower jaw fixed; frothy saliva, tinged with blood, issued from the mouth, and at each expiration there was a strong odor of hydrocyanic acid. The muscles of the extremities were relaxed, and there was entire loss of sensibility. Under the free use of the stomach-pump, and artificial respiration and stimulants, the patient slowly recovered, but it was several days before he was able to leave his bed.

A remarkable series of cases of poisoning by cyanide of potassium is reported by Dr. A. B. Arnold, of Baltimore (*Amer. Jour. Med. Sci.*, Jan. 1869, 103), in which a solution of potassium chlorate had been prescribed for a child. In filling the prescription, the druggist used the last portions of potassium chlorate in the bottle from which he dispensed it. A teaspoonful being given to the child, it was almost instantly seized with convulsions, and quickly died. Dr. Arnold then tasted small portions of the solution, and he soon experienced violent symptoms, and narrowly escaped with his life. Finally, the druggist, to show, as he said, that he had made no mistake, took a portion of the prescription, and in a few minutes afterward fell down dead. It was subsequently learned that the bottle from which the chlorate had been dispensed had previously contained cyanide of potassium.

Period when Fatal.—The fatal period in poisoning by hydrocyanic acid is subject to considerable variation; yet it is extremely limited when compared with that of the action of most other poisons. Several instances are recorded in which death took place in from five to ten minutes, and it has occurred in two minutes, and perhaps even within a shorter period. On the other hand, death has been delayed for nearly an hour, even when the quantity of poison taken

was sufficiently great to produce almost immediate insensibility. In fatal cases, however, life is rarely prolonged beyond half an hour: those who survive this period usually entirely recover. In an accident that occurred in one of the hospitals of Paris, by which seven epileptic patients were fatally poisoned by equal quantities of hydrocyanic acid, the fatal period varied from fifteen to forty-five minutes.

Dr. Fagge relates the case of a medical student who took about a drachm and a half of Scheele's acid, and was thereby immediately rendered insensible; but he did not die from its effects until from one hour and a quarter to one hour and a half after it had been taken. (*Guy's Hosp. Rep.*, 1868, 259.) This is the most protracted case in this respect yet reported.

Fatal Quantity.—That similar quantities of prussic acid do not always produce the same result is well illustrated in the instance of the Parisian epileptics just mentioned. The quantity of the poison taken by each of these patients is stated by most toxicological writers, on the authority of Orfila, to have been equivalent to about two-thirds of a grain of the anhydrous acid; but it appears from more recent statements (*Braithwaite's Retrospect*, xii. 125) that the quantity actually taken by each was equivalent to five grains and a half of the real acid. An instance in which about two grains of the acid caused death has already been cited. In a case reported by Mr. Hicks, a solution containing *nine-tenths* of a grain of the pure acid proved fatal to a healthy woman, aged twenty-two years, in from fifteen to twenty minutes. This seems to be the smallest fatal quantity yet recorded. Smaller quantities have, however, in several instances produced most dangerous symptoms. Several cases are reported in which doses of only about five grains of cyanide of potassium caused death.

On the other hand, Mr. Bishop has related a case in which a man entirely recovered after having taken at a dose forty minims of a solution containing one grain and a third of anhydrous prussic acid. (*Lancet*, London, Sept. 1845, 315.) In this case the patient, according to his own account, remained sensible for at least two minutes after taking the poison. When first seen by Mr. Bishop, about ten minutes after the occurrence, he was senseless, the countenance ghastly pale, face swollen and covered with perspiration, the respiration slow and labored, the eyes fixed and glazed, the pupils

dilated, and the whole body in a rigid state. The treatment consisted in cold affusion, ammonia, emetics, and bleeding. So, also, Dr. Christison has reported a case in which a gentleman recovered after having taken a solution equivalent to between a grain and a half and two grains of the anhydrous acid. And in a case already cited, that reported by Mr. Burnam, recovery followed even after 2.4 grains of the pure acid in solution had been swallowed. In this case, however, as well as in that reported by Dr. Christison, active remedies were almost immediately employed.

Treatment.—On account of the rapid action of hydrocyanic acid when taken in poisonous quantity, it rarely happens that treatment can be resorted to in time to be of much service. The remedies consist chiefly in the exhibition of stimulants; but certain chemical antidotes have also been advised.

The exhibition of the *vapor of ammonia* has been highly recommended, and several instances are reported in which its use was attended with great advantage. It has also been proposed to administer a solution of ammonia diluted with water; but in this form, according to Orfila, it is of no service. *Chlorine*, administered either in the form of vapor or taken internally, has also been strongly advised. It may be used in the form of a weak solution of hypochlorite of lime or of the corresponding sodium salt. The gas is readily obtained by acting on either of these salts with diluted hydrochloric or acetic acid. From experiments on inferior animals, Orfila was led to believe that chlorine was the most efficient antidote yet proposed. It need hardly be added that great caution should be exercised in its administration.

Cold affusion, first recommended by Herbst, has perhaps on the whole been found the most efficient remedy hitherto employed in the human subject. Its use should be accompanied by the exhibition of the vapor of chlorine or ammonia. In several instances of recovery, in which this treatment was employed, it was apparently the means of averting death. Artificial respiration was strongly insisted on by the late Dr. Pereira. He successfully employed it in experiments on animals. Stimulating injections, as well as blood-letting, have also been advised. The latter should be resorted to with great caution. In Dr. Warnek's case of recovery, one hour after a large dose of cyanide of potassium had been taken, the stomach was repeatedly washed by means of the stomach-pump

with tepid water, until the washing no longer had the odor of the poison.

As a *chemical* antidote, it has been suggested by Messrs. Smith, of Edinburgh, to administer a solution of a mixture of the sulphates of the protoxide and sesquioxide of iron (ferrous and ferric sulphates), quickly followed by a solution of carbonate of potassium. A mixture of this kind produces with hydrocyanic acid Prussian blue, which is inert, being insoluble. In experiments on animals, this treatment was quite successful. Even if this antidote be at hand, it should never be relied on to the exclusion of stimulants and cold affusion.

As a *physiological* antidote in poisoning by hydrocyanic acid, Preyer has strongly advised the hypodermic injection of atropine. He found that rabbits to which atropine had previously been administered exhibited a surprising immunity to the action of hydrocyanic acid. But Prof. Boehm and A. Knie, from experiments chiefly on cats, deny the antidotal action of this substance.

Post-mortem Appearances.—These will, of course, depend somewhat on the length of time the individual survived after taking the poison, and also the period that has elapsed since death. The face is usually pale, but often livid, the eyes glistening and staring, the lips blue, the jaws firmly closed, and the extremities soon become rigid. The blood throughout the body is fluid, and generally of a dark or bluish color, but sometimes cherry-red; the venous system is turgid; the arteries are nearly empty; the liver, and in some instances the lungs, much congested. The stomach, other than so far as cadaveric changes have taken place, is generally natural. It need hardly be observed that neither of these appearances is peculiar to death from hydrocyanic acid.

In poisoning by hydrocyanic acid, the blood exhibits no characteristic spectrum, but simply that of oxyhæmoglobin. (C. A. MacMunn, *The Spectroscope in Medicine*, 1880, 89.) If, however, hydrocyanic acid or an alkaline cyanide be added directly to the blood, and the mixture gently warmed, it presents under the spectroscope, as observed by Preyer, a single broad absorption band somewhat similar to that of reduced hæmoglobin, only that it extends somewhat nearer to the violet end of the spectrum, and this portion of it is the darkest.

One of the most striking characters in death from this poison is

the exhalation of the peculiar *odor* of the acid. This is sometimes emitted from the corpse, even before any dissections are made, and, at least in recent cases, is nearly always exhaled when the stomach or thoracic cavity is opened; and it is often detected in the blood throughout the body. As, however, hydrocyanic acid is very volatile, and also readily undergoes decomposition, it may in a little time so far disappear from the body that its odor can no longer be recognized. Moreover, the odor of the acid is liable to be masked by the presence of other odors. In a singular case related by Prof. Casper, however, in which a woman had poisoned herself with a mixture of prussic acid and a variety of essential oils, and the body diffused a *sweet odor*, on opening the stomach such a powerful aroma of bitter almonds came forth *as almost to stupefy every one present.* In several reported instances in which this character was *not* observed in the stomach, a subsequent chemical analysis revealed the presence of very notable quantities of the poison, in one case even so much as one grain of the anhydrous acid. In Dr. Sewell's case, in which seven drachms of the medicinal acid had been taken, he failed to detect the odor of the poison upon applying his nose to the mouth of the deceased, very soon after death. And in the case related by Mr. Hall, he failed to observe the slightest odor of the poison, even in the most forcible expirations of the patient, only some six or eight minutes after about two grains of the acid had been taken, followed by death in less than twenty minutes.

In a very profound but non-fatal case recently reported by Dr. G. W. Maser (*Med. Record*, June, 1884, 711), the *odor* of the acid was observed in the breath of the patient for several days after the poison had been taken.

In the case reported by Hufeland, already mentioned, the body exhaled the odor of the acid on the day following death. The countenance was pale and composed, the eyes glistening, spine and neck stiff, and the back livid. The blood was fluid, bluish in color, and throughout the body emitted a very strong odor of the poison. The vessels of the brain, as well as the liver and lungs, were gorged with blood; the arteries were empty, the veins distended, and the mucous membrane of the stomach and intestines reddened.

In the cases of the seven Parisian epileptics, no odor of the poison was perceived in any part of the body twenty-four hours after death. The lips, face, and head were bloated and of a violet

color; the back livid; frothy blood escaped from the mouth and nostrils; the eyes were closed, and the body rigid. The stomach was highly injected; the liver, spleen, and kidneys much gorged with black blood; the arteries empty, and the veins turgid. In Mr. Hicks's case, in which only nine-tenths of a grain of the acid was taken, the odor of the poison was plainly perceived on opening the chest, and was also strongly emitted from the contents of the stomach, although the examination was not made until ninety hours after death.

In a case examined by M. Buchner (*Amer. Jour. Pharm.*, 1869, 465), the blood was of a clear cherry-red color, and preserved this tint for several days. At the end of five days it was still perfectly liquid, and some weeks elapsed before it gelatinized. When preserved in stoppered bottles, it resisted putrefaction for a long time, but the red corpuscles were destroyed in a few days. It presented *no odor* of prussic acid, but when diluted with water and distilled, the first portions of the distillate possessed a distinct odor of the poison, and gave positive results with the usual tests. By this means the acid was detected even after the lapse of fifteen days.

Chemical Properties.

General Chemical Nature.—Anhydrous hydrocyanic acid (HCy) is a colorless, very volatile, inflammable liquid, of a peculiar odor. It readily mixes in all proportions with alcohol and water. The pure acid has a specific gravity of 0.706, and boils at 26.6° C. (80° F.), yielding a combustible vapor.

The medicinal acid is usually obtained by distilling, at a moderate heat, a solution of ferrocyanide of potassium, K_4FeCy_6, with dilute sulphuric acid, and collecting the product in water, contained in a cooled receiver. The reaction is as follows: $2K_4FeCy_6 + 6H_2SO_4 = 6KHSO_4 + K_2Fe_2Cy_6 + 6HCy$. The commercial acid, when pure, has a very feeble acid reaction, and a density varying with its strength; when it contains about three per cent. of the acid, its specific gravity is about 0.998.

When hydrocyanic acid is brought in contact with a solution of an alkaline hydrate, both the acid and alkaline compound undergo decomposition, with the formation of a salt, or cyanide, of the metal, and the production of water; thus: $KHO + HCy = KCy + H_2O$. These salts are freely soluble in water; they are readily decomposed by acids, with the evolution of free hydrocyanic acid. When ex-

posed to the air, either in their solid state or in solution, they slowly absorb carbonic acid, and thus become changed into carbonates, the eliminated prussic acid being dissipated in the form of vapor. The cyanides of the metals proper, unlike those of the alkalies, are for the most part insoluble in water; but many of them are freely soluble in a solution of an alkaline cyanide, with the formation of a double salt.

Special Chemical Properties.—It has been claimed by several toxicological writers that the *odor* of hydrocyanic acid serves to detect the presence of smaller quantities of the poison than can be recognized by any of the chemical tests; but this is an error, even in regard to the vapor from perfectly pure solutions of the acid. Nevertheless, under certain conditions, extremely minute quantities of the acid may thus be recognized. We have found, in repeated experiments, that when ten grains of a 1–50,000th solution of the *pure* acid ($=\frac{1}{5000}$ grain HCy) are enclosed for some time in a small test-tube, and the tube then opened, the peculiar odor of the poison is sufficiently marked to be described by persons entirely ignorant of the true nature of the solution. With a similar quantity of a 1–100,000th solution an odor is perceptible, but its peculiar character is lost. It need hardly be repeated that the odor from even strong solutions of the poison may be entirely disguised by the presence of other odors.

There are but few chemical tests to which we resort for the detection of hydrocyanic acid, but these are so characteristic and delicate in their reactions as to leave nothing more to be desired in this respect. Moreover, they are equally applicable for the detection of the *vapor* of the poison. In the following examination of these tests, the fractions employed indicate the quantity of anhydrous prussic acid in solution in one grain of pure water. The results, unless otherwise stated, refer to the behavior of one grain of the solution.

1. *Silver Nitrate.*

Nitrate of silver throws down from solutions of free hydrocyanic acid, and of soluble cyanides, a white amorphous precipitate of cyanide of silver, AgCy, which is insoluble in the fixed caustic alkalies, and only sparingly soluble in ammonia, but readily soluble in the alkaline cyanides. Cold nitric acid fails to dissolve it, but it is soluble in the hot concentrated acid; hydrochloric acid decomposes

it with the formation of chloride of silver and the evolution of hydrocyanic acid.

1. $\frac{1}{100}$ grain of hydrocyanic acid, in one grain of water, yields a very copious precipitate, which does not entirely disappear when the mixture is heated with several drops of strong nitric acid.
2. $\frac{1}{1000}$ grain yields a copious precipitate, which readily dissolves on the addition of a drop of strong ammonia; but dissolves with difficulty, in the mixture, in several drops of warm nitric acid.
3. $\frac{1}{10,000}$ grain: a quite good flocculent precipitate.
4. $\frac{1}{25,000}$ grain yields no immediate precipitate, but in a very little time the mixture becomes turbid, and soon there is a very satisfactory deposit.
5. $\frac{1}{50,000}$ grain: after a little time a very distinct opalescence, and soon a very perceptible deposit.
6. $\frac{1}{100,000}$ grain: in a few minutes the mixture becomes very distinctly turbid.

Fallacies.—Nitrate of silver also produces white precipitates in solutions of free hydrochloric acid, of chlorides, carbonates, phosphates, tartrates, and some other salts, and also with various kinds of organic matter. These precipitates, however, except that from chlorine, are readily soluble in strong nitric acid, in which they differ from the cyanide compound. The chloride of silver readily darkens when exposed to light, whereas the cyanide remains unchanged in color; again, the former salt is readily soluble in ammonia, whilst the latter is not, unless present only in very minute quantity. Tolerably strong solutions of iodides and bromides, and of their free acids, yield with nitrate of silver yellowish-white precipitates; from dilute solutions, however, these precipitates, in regard to color, might readily be mistaken for the cyanide compound, especially when they are obtained from organic mixtures: like the cyanide deposit, they are nearly insoluble, or dissolve with difficulty, in cold nitric acid.

The cyanide of silver is readily distinguished from all other precipitates produced by this reagent, in that when thoroughly dried and heated in a narrow reduction-tube it undergoes decomposition with the evolution of cyanogen gas, which, when ignited, burns with a rose-colored flame. If this decomposition be effected in a small tube, which after the introduction of the dried cyanide has been drawn out into a very narrow capillary neck, beginning something

less than an inch above the cyanide compound, the 1–100th of a grain of the salt will yield satisfactory results. For the success of this experiment it is essential that the cyanide be thoroughly dried before being introduced into the tube.

Vapor of Hydrocyanic Acid.—When the vapor of prussic acid is received on a drop of nitrate of silver solution, the latter becomes coated with a white film of cyanide of silver, which, especially from dilute solutions of the acid, is crystalline, and most abundant along the margin of the drop. In its behavior with reagents this deposit has the properties already described. This test may be applied by placing a drop of the acid solution in a watch-glass, and covering the latter with a similar inverted glass, containing a small drop of the silver solution. By this method one grain of the acid solution yields as follows:

1. $\frac{1}{100}$ grain of hydrocyanic acid, in one grain of water: an immediate cloudiness is observed in the silver solution, and in a very little time there is a quite copious white deposit. Under the microscope, the deposit has the appearance of an amorphous mass, but if broken up with the point of a needle it will be found to consist of very small but distinct crystals. If the watch-glass containing the poison be first placed on the stage of the microscope and then covered by the glass containing the silver solution, the formation of the crystals may, at least for a time, be observed.
2. $\frac{1}{1000}$ grain: an immediate cloudiness appears in the reagent solution, and soon there is a quite good, white film. If its formation be observed under the microscope, the crystals will be found to form more slowly and become somewhat larger than in 1.
3. $\frac{1}{10,000}$ grain: in a little time a cloudiness appears, and after a few minutes there is a quite good deposit, which consists principally of irregular crystals, varying from the 1–1000th to the 1–2000th of an inch in length, of the forms illustrated in Plate IV., fig. 1. Usually, small granules, prisms, and needles form along the margin of the drop.
4. $\frac{1}{25,000}$ grain: after a little time the margin of the silver solution becomes white, and soon there is a good crystalline deposit.
5. $\frac{1}{50,000}$ grain: when a very *small drop* of the reagent solution is employed, crystals appear in less than two minutes, and before long there is a very satisfactory deposit.

6. $\frac{1}{100,000}$ grain: after a few minutes crystals can be seen with the microscope, and after some minutes they are quite evident to the naked eye. The deposit is confined to the margin of the drop, and chiefly consists of granules, small prisms, and needles, Plate IV., fig. 2. So far as the evidence of the presence of hydrocyanic acid is concerned, this quantity furnishes as unequivocal results as any larger amount. The formation of the deposit is much facilitated by applying the warmth of the hand to the watch-glass containing the acid solution.

It need hardly be observed that if the silver solution becomes nearly dry from evaporation, crystals of nitrate of silver may separate; but these have a very different form from those of the cyanide, and, moreover, they immediately disappear on the addition of a very small drop of water, whilst the cyanide crystals are almost wholly insoluble in this liquid.

The vapors of chlorine, bromine, and iodine, and of their hydrogen acids, also yield white or nearly white films with a solution of nitrate of silver. The deposits from all these substances, however, are *amorphous;* whereas the cyanide compound is always *crystalline*, even when obtained from complex organic mixtures of the acid, provided sulphuretted hydrogen, or some other gaseous substance which also produces a deposit with the reagent, is not present. The odor of these substances, as well as that of hydrocyanic acid, would generally suffice to determine the true nature of the film produced by these various vapors, even without the aid of the microscope. The deposits produced by the vapors of bromine and iodine have a faint yellowish-white color. It may be remarked that the vapors of chlorine and of hydrochloric acid generally cause the dispersion of the silver solution, so that it trickles down the inside of the inverted watch-glass; and the films produced by them are quite thin, even when occasioned by the pure gases.

2. *Iron Test.*

When a solution of free hydrocyanic acid is treated with a solution of potassium or sodium hydrate, and then with a solution of *ferrous sulphate* which has been exposed to the air and contains some *ferric sulphate*, it yields a precipitate of *Prussian blue*, $Fe_4 3FeCy_6$, mixed with more or less monoxide and sesquioxide of iron: this mixture may have either a yellowish-brown, greenish, or bluish color, the hue

depending upon the relative quantities of the iron compounds present. On treating this mixture with a few drops of hydrochloric or sulphuric acid, the oxides of iron dissolve, while the Prussian blue remains in the form of a deep blue deposit, it being insoluble in the acid. Should the hydrocyanic acid already exist in the form of an alkaline cyanide, the addition of the potassium or sodium solution should be omitted. In a solution of free prussic acid, the iron compounds alone produce no change.

The object of the addition of the free alkali in the above process is to convert the free hydrocyanic acid into an alkaline cyanide. When this salt is then treated with the ferrous and ferric sulphates, a double decomposition takes place, in which the alkaline cyanide becomes changed into potassium sulphate, and the iron sulphates into cyanides of iron; thus: $18KCy + 3FeSO_4 + 2Fe_2 3SO_4 = 9K_2SO_4 + 3FeCy_2 + 2Fe_2Cy_6$; the elements of the iron cyanides then coalesce to form Prussian blue ($3FeCy_2 + 2Fe_2Cy_6 = Fe_4 3FeCy_6$). It is thus obvious that the presence of both the iron salts is necessary for the production of the blue compound. The oxides of iron precipitated by any excess of the alkali employed are dissolved by the hydrochloric or sulphuric acid added, as chlorides or sulphates of iron.

In very dilute solutions of hydrocyanic acid, the test fails to produce an immediate precipitate; but the liquid, after the addition of the mineral acid, immediately acquires a greenish color, and after a time deposits flakes of the blue compound. Such solutions also require a proper adjustment of the alkali and iron solutions. A large excess of the alkali will decompose the Prussian blue, while a similar excess of the iron mixture produces with hydrochloric acid a yellow liquid which may hold in solution a small quantity of the blue compound. When, therefore, the addition of hydrochloric acid produces a yellow solution from which no Prussian blue separates, even after a time, the experiment should be repeated with a less quantity of the iron solution before pronouncing hydrocyanic acid entirely absent. There is no difficulty in the application of the test, except in very dilute solutions of the poison. In no case should any inference be drawn from the color of the precipitate prior to the addition of the mineral acid, since it may have a bluish color even in the absence of prussic acid.

When *one grain* of a *solution* of hydrocyanic acid is treated as above, it yields the following results:

1. $\frac{1}{100}$ grain of the pure acid yields a very copious deposit of Prussian blue.
2. $\frac{1}{1000}$ grain: a very good deposit.
3. $\frac{1}{5000}$ grain: a greenish-blue, flocculent precipitate and a greenish solution; after a time, the deposit increases in quantity and acquires a deeper blue color. Solutions dilute as this, especially when only a single drop is operated upon, require a proper adjustment of the reagent solutions: when these are very strong, only a very small drop of each should be employed.
4. $\frac{1}{10,000}$ grain: with a very small quantity of the reagent solutions, yields a quite perceptible greenish-blue, flocculent precipitate, with a greenish solution; after the mixture has stood some little time, the result is perfectly satisfactory.
5. $\frac{1}{25,000}$ grain yields just perceptible greenish flakes, and, after a few hours, a quite distinct deposit, which, when examined by a hand-lens, has a well-marked blue color.

The production of a blue precipitate insoluble in hydrochloric acid by this test is perfectly characteristic of hydrocyanic acid, or at least of a cyanide. At the same time, the reaction is not interfered with by any substance at all likely to be met with in medico-legal investigations.

Vapor of Hydrocyanic Acid.—In the application of this test for the detection of the vapor of the poison, the vapor is received for some minutes on a drop of potassium hydrate solution, by which it will be absorbed as potassium cyanide, without, however, any visible change; the solution is then treated with the iron mixture and hydrochloric acid, in the manner above described. The vapor from one grain of a 1–5000th solution of the poison will, when the manipulations are conducted with great care, yield quite satisfactory results. This, however, is about the limit of the vapor reaction.

This method may be employed to confirm the nature of the cyanide of silver produced by the preceding reagent. For this purpose the washed deposit, placed in a watch-glass, is treated with a drop of hydrochloric acid, and the vapor of the hydrocyanic acid thus eliminated absorbed by a drop of potassium hydrate solution, in the manner just pointed out. By this process the true nature of a much less quantity of the silver precipitate may be fully established than by the method of reduction, heretofore described.

3. *Sulphur Test.*

When a solution of free hydrocyanic acid or of an alkaline cyanide is treated with a solution of yellow sulphide of ammonium, and the mixture gently heated, it gives rise to sulphocyanide of ammonium, NH_4CyS, which, when treated with a ferric salt, yields a deep blood-red solution of sulphocyanide of iron, Fe_26CyS. This reaction was first pointed out in 1847, by Prof. Liebig.

In applying this test, a few drops of the prussic acid solution, placed in a small white dish or watch-glass, are treated with a drop of the ammonium sulphide, and the mixture evaporated at a moderate temperature on a water-bath to near dryness. Should the residue have a yellow color, it is moistened with a drop of water and again evaporated. The cooled residue—consisting of ammonium sulphocyanide, often in its crystalline state, and a white film of sulphur—is then treated with a drop of a colorless solution of ferric sulphate or of ferric chloride, when the mixture will immediately assume, unless very dilute, a very deep blood-red color. If the excess of ammonium sulphide added has not been entirely decomposed or volatilized, the iron reagent will produce a black precipitate of sulphide of iron; this, however, is readily dissolved by a drop of dilute hydrochloric acid, without interfering with the red color of the mixture, unless it is very feeble.

1. $\frac{1}{100}$ grain of hydrocyanic acid, when treated as above, yields a beautiful blood-red solution.
2. $\frac{1}{1000}$ grain yields an orange-colored mixture.
3. $\frac{1}{10,000}$ grain: the final solution has a very satisfactory light orange hue.
4. $\frac{1}{25,000}$ grain yields a mixture having a distinct reddish tint. The color of this mixture is quite well marked when compared with that of the reagents alone.
5. $\frac{1}{50,000}$ grain yields a just perceptible coloration.

The red color produced by this test is immediately discharged by corrosive sublimate, and by nitric acid; but it is unaffected by even very large excess of strong hydrochloric acid, except from very dilute solutions, when it is readily destroyed by an excess of this acid. It is also discharged, to a faint reddish hue, by an alkaline acetate, but immediately restored upon the addition of hydro-

chloric acid; ammonia causes it to disappear, with the precipitation of sesquioxide of iron.

Fallacies.—Ferric salts also strike a deep blood-red color with solutions of *meconic acid.* This color, however, is not discharged by corrosive sublimate, nor is it affected by an alkaline acetate, and it is readily changed to yellow or reddish-yellow by an excess of hydrochloric acid. The reagent also changes *very strong* solutions of the alkaline acetates to a deep dark-red color, due to the formation of ferric acetate: this color, however, is immediately discharged to a faint yellow tint by even a very small quantity of hydrochloric acid. In this connection it may be remarked that both meconic acid and the alkaline acetates are destitute of odor.

The objections just mentioned are the only ones that can reasonably be urged against the sulphur test, and they are readily answered. When, therefore, a suspected solution yields with the test a strong red color, unaffected by large excess of hydrochloric acid, there is no doubt of the presence of a sulphocyanide; yet, should the color be only faint, its disappearance on the addition of the acid would not prove the entire absence of the poison.

Vapor of Hydrocyanic Acid.—The sulphur test may also be applied for the detection of the vapor of the acid, as first suggested by Dr. A. Taylor. For this purpose, a drop of the ammonium sulphide solution, contained in an inverted watch-glass, is exposed to the evolved vapor for some minutes, and then examined in the manner above described.

The vapor evolved from the 1–10,000th of a grain of prussic acid, in one grain of water, will after this method, providing the ammonium solution has been exposed to the vapor from ten to fifteen minutes, yield a very distinct coloration; but the result could hardly be claimed to be satisfactory. It need hardly be added that when the sulphur test is applied in this manner it is free from the fallacies that hold in its direct application to a suspected liquid.

The sulphur test may also be employed to confirm the precipitate produced by the silver reagent. For this purpose, the washed precipitate is treated with a few drops of sulphide of ammonium, and the mixture evaporated, at a gentle temperature, to dryness. In this operation, the cyanide of silver will be decomposed by the ammonium compound, with the formation of silver sulphide and ammonium sulphocyanide. On now treating the dry residue with a

little water, the ammonium salt will dissolve, and the solution, after filtration and concentration, will yield the usual blood-red color when treated with a persalt of iron.

So, also, this test may be applied to the vapor evolved, when the cyanide of silver is decomposed by a drop of strong hydrochloric acid.

Relative Delicacy of the foregoing Tests.—In regard to the relative value, in this respect, of the *Silver* and *Iron* tests, it may be observed that when they are applied to the *vapor* of the poison the former is much the more delicate, while for *solutions* the latter is much the more susceptible. It is true that the silver test will produce a precipitate with a much less quantity of the poison than the iron test will reveal; yet the silver deposit cannot in itself be regarded as peculiar until it yields an inflammable gas when heated in a reduction-tube, for which purpose it requires, with the greatest care, the precipitate corresponding to at least the 1–500th of a grain of the poison, and even the deposit from this single quantity could by no means be collected and confirmed: but the iron test produces a characteristic reaction with one grain of a 1–10,000th solution of the poison.

On the other hand, when applied to the *vapor* of hydrocyanic acid, the iron reaction has its limit with about the 1–5000th of a grain of the acid, whilst the silver test yields a satisfactory result with the 1–100,000th of a grain, in one grain of water. In other words, for solutions the iron test is about twenty times more delicate than the silver test, while for the vapor of the poison the silver reaction is about twenty times more delicate than the iron test.

In regard to the *Sulphur test*, when applied to solutions of the acid, it is somewhat more delicate than the iron reaction, and so also in regard to the detection of the vapor, but in the latter respect it is very much inferior to the silver method. From a review of these tests, it is obvious that should a suspected solution fail to yield a precipitate with silver nitrate, it would be useless to apply either of the other tests; yet it should be remembered that a solution which only yields a faint reaction with the silver reagent may evolve a vapor that will yield with it very satisfactory results.

The comparative value of these tests may be approximatively exhibited as follows:*

Silver test, with	Solutions,	$\frac{1}{500}$ grain;	with	Vapor,	$\frac{1}{100,000}$ grain.
Iron test, "	"	$\frac{1}{10,000}$ grain;	"	"	$\frac{1}{5000}$ grain.
Sulphur test, "	"	$\frac{1}{25,000}$ grain;	"	"	$\frac{1}{10,000}$ grain.

It need hardly be observed that these results are based upon the assumption that the poison is in solution in *one grain of pure water*, and, it may be added, manipulated with care by experienced hands.

Other Tests.—For the detection of hydrocyanic acid, Lassaigne advised to precipitate it by a solution of *Copper Sulphate*, as copper cyanide; but in every respect this test is inferior to those already mentioned.

Mercurous Nitrate produces in solutions of free hydrocyanic acid, and of alkaline cyanides, a dark gray or nearly black precipitate of finely divided metallic mercury. This reaction serves to distinguish hydrocyanic acid and its simple salts from hydrochloric acid and its compounds, which yield with the reagent a *white* precipitate of mercurous chloride, or calomel. The application of this test, for this purpose, would of course be unnecessary if the iron or sulphur test has been applied.

Schönbein's Test.—This consists in moistening a slip of guaiacum-paper with a solution of copper sulphate, and exposing it to the action of hydrocyanic acid, when it will immediately assume a deep blue color. The guaiacum-paper is prepared by steeping filtering-paper in about a three per cent. solution of guaiacum resin, and drying it. For the copper solution, one part of the sulphate may be dissolved in five hundred parts of water. At the moment of use, the test-paper is moistened with the copper solution and then exposed to the hydrocyanic acid, either diffused in the air as vapor or dissolved in water. M. Schönbein states that the delicacy of this reaction is such that even one part of the vapor of the acid in 120,000,000 parts of air will yield the blue coloration. This reaction, however, is not peculiar to hydrocyanic acid, since ozone, chlorine, and several other vapors produce a similar coloration.

Separation from Organic Mixtures.

As hydrocyanic acid is liable to be rapidly dissipated in the form of vapor, and even to undergo spontaneous decomposition, the examination of a mixture in which its presence is suspected should not be delayed. The same method of research will apply equally to

suspected articles of food or medicine, the matters vomited, and the contents of the stomach. Before resorting to the application of any chemical test, the suspected mixture should be carefully examined in regard to its odor; but it must be borne in mind that mixtures of this kind may contain a very notable quantity of the poison without emitting its peculiar odor.

Examination for the Vapor.—For this purpose, the suspected mixture is placed in a glass jar or any similar vessel, and the mouth of the vessel then covered by an inverted watch-glass in which has been previously placed a drop of nitrate of silver solution. Sooner or later, even if only a minute trace of the vapor is being evolved from the mixture, the silver solution will acquire a white incrustation of cyanide of silver. Any deposit thus produced is then examined under the microscope: at the same time, the mouth of the bottle should be closed by a cork, or by another watch-glass containing a drop of the silver reagent. Should the microscope reveal the presence of crystals of the forms already described, these will fully establish the presence of the poison, since there is no other substance that will yield similar results. Should, however, the deposit be amorphous, it may still, in part at least, be due to the cyanide; but it might be due to the presence of chlorine, or possibly to the vapor of bromine or of iodine. Under these circumstances, the true nature of the deposit, if cyanide of silver, may be established either by the iron or the sulphur test in the manner already indicated. One or both of these latter tests should also be applied directly to the suspected mixture, even in case the silver reaction is satisfactory.

Should the silver solution, after an exposure of several minutes, fail to indicate the presence of the poison, the suspected mixture should be occasionally agitated by shaking the bottle, and the application of the reagent be continued for half an hour or longer. If there is still no evidence of the presence of the poison, it is not likely that it would be detected by this method, even if applied for several hours; yet it must not be concluded that the poison is entirely absent even in its free state, since it may be strongly retained by organic substances. In case the silver reagent should fail to receive a deposit, it would of course be useless to apply either of the other tests for the vapor.

Method by simple Distillation.—After testing the suspected liquid in regard to its reaction and setting apart a small portion, for future

examination if necessary, the remaining portion is placed in a retort having its neck slightly inclined upwards and connected, by means of a bent tube and corks, with a Liebig's condenser, the lower end of which opens into an ordinary receiver. In the absence of Liebig's condenser, the retort may be connected directly with a well-cooled receiver. The liquid is then distilled at a moderate heat, by means of a water-bath, until about one-eighth of the fluid has passed over into the receiver. On account of its volatile nature, any free hydrocyanic acid originally present in the liquid will now be found in the distillate, which may be examined in the usual manner.

If prussic acid is thus obtained and the original liquid was destitute of a strongly acid reaction, then there is little doubt that the poison was present in its free state; yet it may have existed as an alkaline cyanide, but it could not have been in the form either of a ferro- or sulpho-cyanide. To determine whether it existed in its uncombined state or as an alkaline cyanide, a portion of the reserved fluid is treated with a mixture of ferrous and ferric sulphates: if this yields no change, the hydrocyanic acid is free; but if it yields Prussian blue, either at once or after the addition of hydrochloric acid, then the poison exists in the form of a cyanide. If the liquid under examination has an alkaline reaction, the poison, if present, will of course be in the form of a cyanide, even though originally added in its free state.

Should the mixture in the retort evolve either hydrochloric acid or sulphuretted hydrogen, this will collect with the distillate, and interfere with the reaction of the silver test; neither of these substances, however, would prevent the normal reaction of either the iron or the sulphur test. Hydrochloric and hydrocyanic acids may be separated by redistilling a portion of the distillate with powdered borax or carbonate of calcium, which will retain the chlorine compound, but not hydrocyanic acid.

Distillation with an acid.—If the above method fail to reveal the presence of the poison, the contents of the retort, after the addition of water if they have become thick, are acidulated with sulphuric acid, and distilled as before. Any simple cyanide present would now evolve the whole of its cyanogen in the form of hydrocyanic acid. Should it at first be suspected that the poison existed as an alkaline cyanide, this method of distillation may at once be adopted. It must be remembered, however, that by this process a ferrocyanide,

such as potassium ferrocyanide, or yellow prussiate of potash, would also evolve prussic acid; and the same may also be true, if the distillation is continued for some time, in regard to the sulphocyanide of potassium, which exists in small proportion in human saliva.

The source of the poison obtained in the distillate when an acid has been employed may be determined by treating a portion of the reserved liquid, after filtration if necessary, with a few drops of hydrochloric acid, and stirring the mixture for some minutes, and then adding a solution of ferric chloride. If the liquid thus treated contained a simple cyanide, the iron reagent will produce no visible change, since the cyanide would have been converted by the hydrochloric acid added into a chloride, and the whole of the prussic acid evolved; but if it contained a ferrocyanide or a sulphocyanide, this will remain, and yield either a deposit of Prussian blue or a deep red solution, as the case may be. As commercial cyanide of potassium is liable to be contaminated with ferrocyanide of potassium, traces of the latter might be present in poisoning by the former.

If there is reason to suspect that free hydrocyanic acid or cyanide of potassium is present with ferrocyanide of potassium, they may be separated, according to Otto, in the following manner. The mixture is treated with a solution of ferric chloride as long as a precipitate is produced, by which the ferrocyanide compound will be converted into Prussian blue; sodium carbonate is then added, until the mixture exhibits an alkaline reaction, then tartaric acid, until it shows a feebly acid reaction; it is then distilled in the ordinary manner. By this method ferrocyanide of potassium yields a distillate entirely free from hydrocyanic acid, since it is retained as Prussian blue, which is unaffected by the distillation; but when hydrocyanic acid or an alkaline cyanide is present, the distillate will contain the poison in its free state.

This process is admirably adapted for the separation of free hydrocyanic acid from a ferrocyanide; but when the poison is present in the form of an alkaline cyanide, much or even the whole of it, if only in small quantity, may be retained as Prussian blue. It is true that ferric chloride produces with cyanide of potassium at first only free hydrocyanic acid, sesquioxide of iron, and chloride of potassium; but this mixture will after a little time form more or less Prussian blue. This conversion will, of course, take place at once if the iron reagent contains a ferrous salt.

For the separation of free hydrocyanic acid, cyanide of potassium, and ferrocyanide of potassium, it has also been proposed to distil the mixture without the addition of an acid, when the free prussic acid would pass over with the distillate; the residue in the retort is then filtered, and the filtrate concentrated to a small volume and treated with strong hot alcohol, which will dissolve the cyanide, whilst the ferrocyanide would be precipitated in yellowish-white scales, it being insoluble in this liquid.

For the detection of an alkali cyanide in the presence of a ferrocyanide, W. J. Taylor has recently advised (*Chem. News*, Nov. 1884, 227) to distil an aqueous solution of the mixture with an excess of acid sodium carbonate, when the cyanide will be decomposed with the evolution of hydrocyanic acid, the ferrocyanide remaining unchanged. The evolved hydrocyanic acid may be collected in a solution of ammonium sulphide, which will retain it as ammonium sulphocyanide, readily recognized by its reaction with ferric chloride. According to this author, the presence of potassium sulphate, potassium ferricyanide, potassium sulphocyanide, or of ammonium salts, does not interfere with the reaction.

From the Blood and Tissues.—The methods already described are equally applicable for the examination of any of the fluids or soft solids of the body, in poisoning by prussic acid. Experiments upon animals have shown that the poison, when introduced into the stomach, may be diffused throughout the blood within a few seconds. In the case already cited from Casper, in which a mixture of prussic acid and some essential oils proved fatal to a woman, the distillate obtained from about an ounce of blood from the body gave, with the iron and sulphur tests, very distinct evidence of the presence of the poison: the silver test was not applied. The blood was treated with a small quantity of spirits of wine and phosphoric acid, and distilled until about two drachms of fluid, smelling slightly of bitter almonds, had passed over. In this case, death must have taken place with great rapidity, since the deceased was found lying on the floor, with half a cucumber in one hand and a water-jug in the other. The same writer relates another case, in which an apothecary took, with suicidal intent, an unknown quantity of hydrocyanic acid, and the poison was recovered from the blood, by being distilled, in this instance, with a few drops of sulphuric acid. It was also found in the contents of the stomach; but not in the urine contained in the bladder.

Failure to detect the Poison.—On account of its rapidly fatal effects, there is no ordinary poison more likely than hydrocyanic acid to remain in the body at the time of death; yet on account of its ready decomposition and great volatility, there is perhaps none that may more rapidly disappear from the dead body. The time in which a given quantity of the poison may thus entirely disappear from the body, or from any organic mixture, will of course depend upon a variety of circumstances. In a case of suicidal poisoning by hydrocyanic acid mentioned by Prof. Casper, *twenty-six* hours after death no trace of the poison was found in the stomach, but there was present a considerable quantity of *formic acid*, as a result of the decomposition of the prussic acid.

On the other hand, cases are recorded in which the poison was recovered after comparatively long periods. Thus, Dr. Christison quotes a case in which it was detected in a body *seven days* after death, although the corpse had never been buried, and had been for some time lying in a drain. In an instance cited by Dr. Taylor, where a dose equivalent to something over three grains of anhydrous prussic acid proved fatal in about fifty minutes, it was detected both before and after distillation, in the contents of the stomach, *seventeen days* after death. In a more recent case, the acid is said to have been detected in the blood and brain *eleven days*, and in the intestines *fifteen days*, after death. The longest period in this respect yet reported is in a case in which E. Reichardt detected hydrocyanic acid *two months* after death in a case of undoubted poisoning. (*Jour. Chem. Soc. Abst.*, Feb. 1882, 246.) In this instance the iron and the guaiacum-copper tests were applied to the distillate from the organs after addition of tartaric acid, the absence of ferrocyanides and thiocyanates (sulphocyanides) being previously determined.

Quantitative Analysis.—The quantity of hydrocyanic acid present in a pure solution of the poison may be readily determined by precipitating it as cyanide of silver. For this purpose, the solution is treated with a solution of silver nitrate as long as a precipitate is produced; the mixture is then slightly acidulated with a few drops of nitric acid, and the precipitate collected on a filter of known weight, thoroughly washed, dried at 100° C. (212° F.), and weighed. Every one hundred parts by weight of cyanide of silver thus obtained correspond to 20.15 parts of anhydrous hydrocyanic acid.

Section III.—Phosphorus.

History.—This remarkable elementary substance was first discovered by Brandt, in 1669, and received its name from its ready inflammability and from being luminous in the dark. Phosphorus is found in the three kingdoms of nature, but most abundantly as a constituent of bones, in which it exists as phosphoric acid, and this in combination with calcium; it is never found in its free state in nature. In its uncombined state, phosphorus is a most powerful poison, and numerous instances of poisoning by it have occurred, especially since the introduction of friction-matches, and of phosphorus-pastes for the purpose of destroying rats.

Symptoms.—The more usual effects produced by phosphorus, when taken in poisonous quantity, are a feeling of lassitude; gaseous eructations, which have a garlic-like odor, and are sometimes luminous in the dark; burning pain in the stomach and bowels; nausea; violent vomiting; sometimes purging; great thirst; cold perspirations; great anxiety; and a feeble, irregular pulse. The matters first vomited have generally an alliaceous odor, and evolve white fumes, which shine in the dark; similar appearances have also been observed in the fæces, which have even contained solid particles of the poison. The abdomen becomes tender to the touch; the extremities cold; the pulse almost imperceptible; the pupils dilated and insensible; and frequently death is preceded by convulsions. If the patient survive two or three days, jaundice generally manifests itself, usually appearing first in the conjunctiva. The urine is generally albuminous and much diminished in quantity, or it may be entirely suppressed.

In a case of poisoning by this substance related by Dr. Lewinsky, in which a girl, aged twenty-two years, swallowed a portion of phosphorus scraped from a small packet of lucifer-matches, the following symptoms were observed. Soon after taking the poison, the patient experienced a sharp burning pain in the abdomen, followed by vomiting of matters which were observed to be luminous while being ejected from the stomach. Some hours afterward, she was suffering from vomiting and purging; but no odor of phosphorus was perceptible in the excretions. The abdomen was swollen and sensitive on pressure; the tongue white and moist; the pulse normal, and the intellect clear. Vomiting, alternating with hic-

cough, continued unceasingly until the third day; but the purging ceased on the second day. On the third day, there were signs of jaundice; the urine was scanty and of a dark color; and the pupils were widely dilated, and nearly insensible to light. On the fourth day, the jaundiced appearance of the face was much increased, and there was collapse and great restlessness, with extreme thirst, and a weak, quick pulse; but the vomiting had abated, a small quantity of blood only being thrown up; convulsions and impaired consciousness then supervened, and death occurred on the sixth day after the taking of the poison. (*Brit. and For. Med.-Chir. Rev.*, Oct. 1859.)

In contrast with the above case may be cited the following, related by Prof. Casper. (*Forensic Medicine*, ii. 100.) A young lady, aged twenty years, took at six o'clock in the evening at least three grains of phosphorus in the form of the officinal electuary. Those around her remarked nothing peculiar; and during the evening she wrote a letter. Later in the evening she seemed to her family to exhale "sulphur" (evidently confounding the vapor of sulphur with that of phosphorus-matches), and complained that the light blinded her, but made no complaint whatever of pain. During the night, which she passed sleeplessly, she vomited *once*, and died quite peacefully at six o'clock in the morning, just twelve hours after taking the poison.

The following case, in which about three grains of phosphorus had been taken, is reported by Dr. S. O. Habershon. (*Medico-Chir. Trans.*, 1867, 87.) A woman, aged twenty-eight, in good health, drank by mistake a mixture containing some rat-poison. Immediately after taking the draught the woman complained of severe burning pain in the mouth and throat; the breath was phosphorescent; violent vomiting and purging soon followed. In two hours these symptoms subsided, and there was neither dyspnœa nor cough. On the morning of the sixth day, she was seized with violent pain in the loins; the skin was moist, but the face and extremities were cold; the conjunctiva and the whole body were slightly jaundiced; the pupils were natural; the lips parched; the tongue dry. The abdomen was somewhat distended and tympanitic; the liver was enlarged; no pulse could be felt at the wrist. Some hours later, sudden vomiting of a dark grumous fluid came on, and the patient died almost immediately, five days after taking the poison.

Dr. F. P. Henry has recently reported a case (*Medical Times*,

Phila., June, 1883, 696), in which a man, aged twenty-two, drank a solution of phosphorus obtained by soaking the heads of a box of matches in water. Fifteen minutes after swallowing the solution, the patient experienced a burning sensation in the stomach, which, after a time, became excruciating. Copious and repeated attacks of vomiting then ensued, and there was excessive thirst. On the next day there was a loose discharge from the bowels. These symptoms were followed by tenderness over the liver; severe pain in the abdomen; pulse full and strong; and the urine contained considerable albumen. Some days later, there was intense jaundice; one clay-colored stool; and the bladder was relieved by catheter of forty-eight ounces of urine, which contained bile-pigment in large quantity, and had the odor of phosphorus. The man died one week, less fourteen hours, after taking the poison.

In a case related by Dr. Stevenson, a woman took a quantity of phosphorus estimated at something less than two grains, and, except slight gastric pain, no marked symptoms appeared for three and a half days. The usual symptoms then developed, followed by death on the seventh day. (*The Practitioner*, Dec. 1882, 432.)

A singular case is related by Dr. Landerer, in which a woman, in order to come into the possession of a large inheritance, poisoned a boy, aged fifteen years, by introducing the ends of phosphorus-matches into his *rectum*. The boy died the same night, with severe pain and inflammation of the rectum. (*Medical News*, May, 1882, 544; from *Archiv d. Pharm.*, 1882.)

The inhalation of the *vapor* of phosphorus by an apothecary, who applied in his cellar some phosphorus-paste to some wheat to be used for the destruction of field-mice, caused complete prostration, and death within a week. (*Amer. Jour. Pharm.*, Jan. 1873, 16.)

Period when Fatal.—In fatal poisoning by phosphorus, death usually takes place in from one to five days. One of the most rapidly fatal cases yet recorded is that related by Prof. Casper, cited above, in which death occurred in *twelve hours*. In another case, the phosphorus from forty-two matches proved fatal in thirteen hours. And in a case quoted by Dr. Christison, the taking of a portion of lucifer-match composition was followed by vomiting, pain in the abdomen, anxiety, restlessness, excessive thirst, and death in fifteen hours. (*Op. cit.*, 151.) Dr. Habershon cites a case, related by Dr. Tüngle, fatal in *half an hour*. In an instance reported by Dr.

Flachsland, a young man, aged twenty-four years, took an unknown quantity of the poison, spread on bread with butter. He soon experienced violent pain in the stomach and bowels, and intense vomiting, which continued the following day: after the use of clysters, he passed small fragments of phosphorus, which were luminous in the dark and burned spots in the bed-linen. Death ensued in *forty hours* after the poison had been taken. (*Medizinisch-Chirurgische Zeitung*, 1826, iv. 183.) Orfila, in quoting this case (*Toxicologie*, 1852, i. 84), erroneously states that death took place in four hours.

Among the more protracted cases may be mentioned the following. M. Diffenbach, an apothecary of Biel, as a matter of experiment, took one grain of phosphorus on the 2d of July, 1823. On the 21st of the same month he took two grains, and on the following day increased the dose to three grains. During the evening of the last day he experienced uneasiness and a sense of pressure in the abdomen. These symptoms were succeeded by violent and incessant vomiting, convulsions, delirium, and partial paralysis, and death ensued on the 29th of the month, or the *seventh day* after the last dose of poison had been taken. (*Revue Médicale*, 1829, iii. 429.) In another case, reported by Dr. Concato, life was prolonged *eleven days*. And in a case quoted by Dr. Beck, in which a young man took one grain and a half of phosphorus, death did not occur until the *twelfth day* after the taking of the poison. (*Med. Jur.*, ii. 511.)

Fatal Quantity.—The effects of a given quantity of phosphorus will depend much upon the state in which it is taken. A child, two years and a half old, died from swallowing the phosphorus contained on eight friction-matches; and a child, two months old, is said to have died from the effects of two such matches. (Wharton and Stillé, *Med. Jur.*, 505.) The quantity of the poison taken in the last-mentioned instance could not have much exceeded the *fiftieth* of a grain. In a case quoted by Dr. Taylor, *one-eighth* of a grain destroyed the life of a lunatic. In another instance, the composition from thirty or forty lucifer-matches, administered with milk, proved fatal to a woman in less than forty-eight hours. (*London Chem. News*, April, 1860, 207.) Again, Dr. Christison quotes the case of a patient, affected with lead-palsy, who died in about two days from the effects of considerably less than a grain of the poison, taken in the form of an emulsion.

On the other hand, a case is related in which a child swallowed nearly a teaspoonful of phosphorus-paste, prepared for killing rats, and, under the free administration of magnesia, entirely recovered. (*U. S. Dispen.*, 1865, 644.) The quantity of phosphorus taken in this case probably exceeded one grain. In a case quoted by Dr. Taylor, a young woman swallowed the phosphorus obtained from about three hundred matches—equal to rather less than five grains of the poison—and recovered without any very severe symptoms. (*On Poisons*, 345.) These are the most remarkable instances of recovery, after the taking of this poison, yet recorded; in fact, very few cases of recovery have as yet been reported.

TREATMENT.—If there is not already free vomiting, it should be induced by the exhibition of an emetic, sulphate of copper, in repeated doses, being preferred for this purpose. Calcined magnesia, suspended in large draughts of any demulcent liquid, may then be freely administered: this may serve to neutralize any oxide of phosphorus remaining in the stomach. Instances are related in which this treatment was employed with great success. It has been proposed to administer the magnesia in suspension in chlorine water; but more recent experiments on animals have indicated that this mixture has no special advantage. Since phosphorus is somewhat soluble in fatty substances, the administration of these should be avoided. If the poison has passed into the intestines, purgatives may be used with advantage.

As an antidote in acute phosphorus poisoning, *oil of turpentine* has been advised, and the results of numerous experiments upon animals have been adduced in its favor. In the hands of other experimentalists, however, this substance has proved wholly inert. It is now generally admitted that only certain kinds of turpentine are antidotal, that which is old and has not been rectified being the most efficient. So, also, the soluble salts of copper have been recommended. Phosphorus, in contact with a solution of this metal, is quickly coated with a black deposit, said to be a phosphide of copper. Prof. Bamberger claims that this antidote is more efficient than oil of turpentine; whereas G. H. Roessingh, from repeated experiments, holds the opposite view. (*New Sydenham Soc.*, 1873, 440.) Among other agents that have been proposed as antidotes may be mentioned animal charcoal, oxygenated water, peroxide of hydrogen, and the slow injection of oxygen into the veins.

Post-mortem Appearances.—The contents of the stomach have in some instances evolved white fumes, having an alliaceous odor, and being luminous in the dark. The lining membrane of the stomach is generally much inflamed, and has even presented a gangrenous appearance; these appearances may extend throughout the intestines, which are often much contracted. The liver, spleen, and kidneys are often highly reddened, the lungs gorged with blood, the heart empty, and the brain congested. The blood throughout the body is usually dark-colored and remarkably fluid.

In the more protracted cases, the skin frequently presents a jaundiced appearance, and there is generally fatty degeneration of the liver, kidneys, and heart; this change may extend to most of the soft organs of the body. The liver is generally enlarged, of a yellow color, and soft and inelastic; in some cases this organ was found atrophied.

In the case fatal in twelve hours, related by Prof. Casper, forty-eight hours after death luminous vapors were observed to issue from the vagina, and a grayish-white vapor smelling strongly of phosphorus continuously streamed from the anus! A very distinct odor of phosphorus also came from the mouth, but without any visible vapor. The stomach itself diffused no odor of phosphorus; and no part of its mucous membrane was either softened or corroded. It contained about six to eight ounces of a bright blood-like fluid, mingled with coagulated milk; no particles of phosphorus could be detected in the stomach, even with a magnifying-glass. The intestines were pale, and presented nothing abnormal. The blood was dirty-red, of a syrupy consistency, and the blood-corpuscles were transparent and deprived of their coloring-matter. The liver, spleen, and kidneys were congested. The bladder was of a livid color, and contained about a tablespoonful of milky urine. The lungs contained but little blood, and the heart was almost completely empty; but the large blood-vessels contained much blood. The meninges were moderately congested, and the brain contained more blood than usual.

In Dr. Lewinsky's case, in which death occurred on the sixth day, the stomach was filled with gas and a blackish-brown fluid; its mucous coat was raised from beneath, and covered with a thick mucus, streaked with dark-brown lines. The intestines contained a blackish-brown, thin, frothy liquid. The bladder was contracted and empty. The cavity of the throat contained a bloody, frothy

mucus, which extended into the bronchial tubes. The lungs were covered with a flaky exudation. The heart was contracted, and its cavities contained fluid blood with a little coagulated fibrin. The structure of the brain was free from blood, but the ventricles contained a drachm of serum. A chemical examination of the stomach and its contents, by Dr. Schauenstein, showed no indication of the presence of phosphorus.

In the case reported by Dr. Flachsland, which proved fatal in forty hours, watery blood flowed in large quantity from the nostrils, and also from the first incisions made into the skin and muscles of the abdomen. The stomach and bowels externally were inflamed; the mucous membrane of the stomach presented a gangrenous inflammation, which extended into the duodenum; the large intestines were contracted to the size of the little finger. The mesenteric glands were hardened, and the spleen and kidneys inflamed.

Dr. Hall Curtis relates a case (*Boston Med. and Surg. Jour.*, April, 1876, 433) in which a man took a quantity of rat-poison, and died from its effects, under the usual symptoms, in forty-six and a half hours. No symptom was observed until eight hours after the poison had been taken, when the man experienced slight pain at the epigastrium. At the autopsy, the heart was found pale and soft; its muscular tissue was slightly yellowish and soft, but not friable; and its cavities contained considerable soft-clotted blood. The liver was normal in size, but both externally and internally it was of a bright golden-yellow color. The kidneys were pale, the tubules indistinct, with a yellowish tinge between the cortical and medullary portions. The brain was normal. Neither the stomach nor the small intestines were inflamed or congested. Examined microscopically, the liver, heart, and kidneys were found in a state of excessive fatty degeneration. Phosphorus was found in the stomach and in the urine.

Chemical Properties.

General Chemical Nature.—Phosphorus, at ordinary temperatures, is a soft, colorless, transparent solid, having a waxy appearance, and a specific gravity, according to Schrötter, of 1.83. It fuses at a temperature of about 44° C. (111° F.), and boils at 290° C. (554° F.). When exposed to the air, it slowly absorbs oxygen, and emits white fumes of phosphorous oxide; at the same time it exhales

a peculiar garlic-like odor, and the fumes are luminous in the dark. Berzelius believed that this luminosity was due to the volatilization of free phosphorus, but, according to Schrötter, it is due to the combination of the phosphorus with oxygen. (*Chem. Gaz.*, xi. 312.) This oxidation, and consequently the luminosity, are prevented by the presence of the vapor of ether, alcohol, turpentine, and of certain other liquids, even when these are present only in minute quantity.

Heated in the open air, phosphorus takes fire at a temperature of about 60° C. (140° F.), and burns with a brilliant white light, evolving dense white fumes of phosphoric oxide. The presence of certain oxidizing agents causes it to inflame at much lower temperatures.

Solubility.—Phosphorus is insoluble in water, but it dissolves to a limited extent in fixed and volatile oils, especially by the aid of heat. It also dissolves to a limited extent in ether, and somewhat more freely in hot naphtha, from which, however, it partially separates on cooling in rhombic dodecahedral crystals. It is freely soluble in chloride of sulphur, and in disulphide of carbon; five parts of the latter liquid dissolve one of phosphorus (Graham). It is insoluble in hydrochloric acid, but warm nitric acid readily oxidizes and dissolves it in the form of phosphoric acid.

When phosphorus is immersed in water and exposed to the action of light, it slowly becomes covered with a white opaque coating, which, according to H. Rose, is nothing more than pure phosphorus, the change being simply due to a change in its state of aggregation. At the same time, however, a little of the phosphorus undergoes oxidation, and is dissolved by the liquid.

Varieties.—Of the several allotropic forms of phosphorus, the *Red or amorphous* variety is the only one that need be mentioned. This form is obtained by heating ordinary phosphorus in an atmosphere of carbonic acid or of any gas that does not act upon it chemically, when after a time it will become converted into a dark-red amorphous mass, from which any unchanged phosphorus may be dissolved by treating the mixture with disulphide of carbon.

This variety of phosphorus differs not only in respect to its physical properties, but also in regard to its physiological effects and chemical properties, from ordinary phosphorus, although its ultimate composition is precisely the same. Thus, it is destitute of odor, and does not become luminous in the dark until heated to about 204° C. (400° F.). Its fusing point is about 249° C. (480° F.); at a tem-

perature of about 260° C. (500° F.) it is reconverted into ordinary phosphorus. It is insoluble in disulphide of carbon, trichloride of sulphur, ether, alcohol, and naphtha; but it is sparingly soluble in oil of turpentine. Moreover, from experiments on animals, it appears to be entirely destitute of poisonous properties.

Special Chemical Properties.—The physical appearance of phosphorus, together with its odor, the production of white fumes when exposed to the air, its ready inflammability, and its phosphorescence in the dark, readily serve to distinguish it in its solid state, even in very minute quantity, from all other substances.

When a mixture containing free phosphorus is gently heated, best by means of a water-bath, in a test-tube, in the neck of which is suspended a slip of filtering-paper moistened with a solution of silver nitrate, the vaporized phosphorus on coming in contact with the silver compound decomposes it, with the production of phosphoric acid and the elimination of metallic silver, which imparts to the paper a brown or black coloration. A very minute trace of the poison will thus manifest itself.

Since, however, there are several other vapors that will blacken a solution of silver nitrate, this change taken alone would not prove the presence of phosphorus. That the result is really due to the presence of phosphorus may be determined by digesting the blackened paper with a small quantity of hot water, precipitating any undecomposed nitrate of silver present by hydrochloric acid, filtering, and examining the concentrated filtrate for phosphoric acid, in the manner hereafter indicated.

When phosphorus in its free state is mixed with diluted sulphuric acid and zinc in a test-tube, or in any convenient vessel, a portion of the hydrogen gas evolved by the action of the acid and zinc unites with the phosphorus with the production of phosphuretted hydrogen gas, which is luminous in the dark, and sometimes spontaneously inflammable. A very small quantity of phosphorus will in this manner evolve a phosphorescent gas for half an hour or longer; and when the experiment is performed in a small, narrow test-tube and in a perfectly darkened room, or better at night, the least visible quantity of the poison will yield very satisfactory flashes of light, which continue to be produced for some time.

If the phosphuretted hydrogen thus evolved, together with the free hydrogen, be conducted through a drawn-out tube, and ignited,

they burn with a greenish flame surrounded by a delicate blue mantle. Paper moistened with nitrate of silver solution and exposed to the unignited gas is immediately blackened. If the gas be conducted into water, it gives rise to white fumes as it escapes from the liquid. With a solution of nitrate of silver, it gives rise to phosphoric acid, which remains in solution, and a black precipitate, consisting of a mixture of metallic silver and phosphide of silver. When conducted into a solution of corrosive sublimate, it produces a yellow or yellowish-white precipitate, which, according to H. Rose, consists of phosphide and chloride of mercury.

1. *Mitscherlich's Method.*

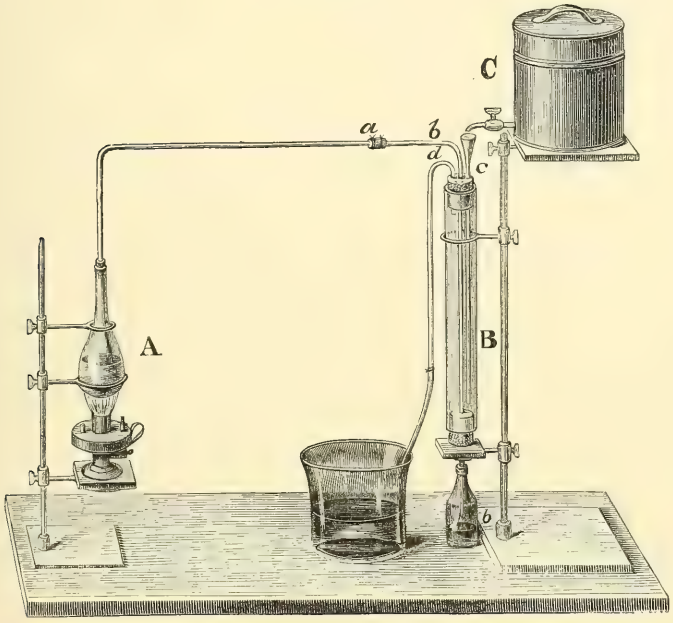
The most delicate method yet proposed for the detection of uncombined phosphorus is that first pointed out by E. Mitscherlich. It consists in distilling the substance containing the phosphorus with diluted sulphuric acid, and conducting the evolved vapors through a glass tube surrounded by a condenser. The vapor of phosphorus is thus condensed, and gives rise to a continuous luminosity, when observed in the dark.

For the application of this method, the phosphorus mixture, after the addition of water if necessary, is acidulated with sulphuric acid and placed in a glass flask, A, Fig. 2. The flask is connected by means of an exit-tube, *a*, with a delivery-tube, *b*, which is bent at a right angle, and after passing through a glass cylinder, B, filled with cold water, terminates in a drawn-out point within a small bottle, which serves as a receiver. The condenser may be readily constructed by taking a glass tube, about twenty inches in length and one inch and a half in diameter, and closing the ends with good corks, the upper of which has three perforations, while the lower has one for the passage of the delivery-tube: the condenser is supplied with cold water from the reservoir, C, the liquid being conducted by a funnel-tube, *c*, to the bottom of the condenser; the warmed water is carried off from the surface of the liquid by a siphon, *d*. Having thus adjusted the apparatus, a dark screen is placed between the flask and the condenser.

On now gently boiling the contents of the flask, while a stream of cold water flows through the condenser, a very distinct and continuous luminosity, usually some inches in length, will be observed in the dark to play up and down the cooled portion of the delivery-

tube. The phosphorus thus distilled collects with the condensed aqueous vapor in the receiver, and imparts to the liquid a strong alliaceous odor. When the quantity of phosphorus is not too minute, a portion of it collects in the receiver in the form of small globules; a portion of it, however, always undergoes oxidation and remains in solution in the distillate, in the form of phosphorous acid, and also,

FIG. 2.



Mitscherlich's apparatus for the detection of phosphorus.

sometimes, as phosphoric acid. The true nature of any globules thus obtained may be determined even by their physical properties.

The presence of phosphorous acid in the distillate may be shown by treating the filtered liquid with a solution of silver nitrate or of mercuric chloride; but as both these reagents produce precipitates with various kinds of organic matter, which if present in the original mixture might distil over, it is always best, when examining a suspected mixture, to convert the phosphorous acid into phosphoric acid before testing. For this purpose, the distillate is treated with a few drops of nitric acid, concentrated to a small volume, filtered if neces-

sary, and then examined by molybdate of ammonium or any of the other tests pointed out hereafter for the detection of phosphoric acid.

When in the examination of a suspected mixture a luminosity has been observed during the distillation, and globules of phosphorus have collected in the receiver, it is unnecessary to examine the condensed liquid. On the other hand, if no luminosity or globules of phosphorus have been obtained, great care should be exercised in regard to any deductions from the detection of a mere trace of phosphoric acid in the distillate, since it may have been carried over mechanically from the mixture submitted to distillation. It may be remarked that it is only when the original mixture contains unoxidized phosphorus that a luminosity and globules of phosphorus will be obtained, as neither phosphorous acid nor phosphoric acid yields either of these results; nor will either of these oxides appear in the distillate, even when present in the original mixture in large quantity, unless they be carried over mechanically with the vapor of water.

Delicacy of this Method.—Mitscherlich distilled five ounces of a mixture containing the *fortieth* of a grain of pure phosphorus, —that is, one part of phosphorus in little less than one hundred thousand parts of the mixture,—and the luminosity continued until three ounces of liquid distilled over, which required about half an hour. In another experiment, he distilled five ounces of a mixture containing one-third of a grain of phosphorus, and obtained such a number of globules of phosphorus in the distillate that one-tenth part of them would have sufficed to establish their true nature.

In one of our own experiments, the *fiftieth* of a grain of phosphorus was distilled with two thousand fluid-grains of water, acidulated with sulphuric acid. As soon as the mixture was brought to the boiling temperature, a phosphorescent light some inches in length appeared in the tube within the condenser, and continued without intermission for thirty-four minutes, at which time the distillation was stopped, and eighteen hundred and twenty grains of fluid had distilled over. The distillate had a strong alliaceous odor, but it contained no globules of phosphorus; it, however, readily furnished evidence of the presence of oxides of phosphorus. The amount of phosphorus that passed through the tube per second, in this experiment, must have been something less than the 1–100,000th of a grain; yet this gave a luminosity many times greater than would have sufficed to recognize its presence with absolute certainty.

Interferences.—It has already been remarked that the presence of certain vapors may entirely prevent the luminosity of phosphorus. Thus, if the mixture subjected to distillation contained alcohol, ether, or oil of turpentine, no luminosity would be observed as long as these distilled over. Alcohol and ether, being very volatile, would soon be separated, and the light would then appear; but this would not be the case in regard to the presence of oil of turpentine: this liquid, however, is not likely to be present in a medico-legal examination for phosphorus, unless it had been given as an antidote. M. Lipowitz has shown that the phosphorescence is also interfered with by the presence of ammonia; but this substance would be neutralized by the sulphuric acid added.

According to Dr. F. Hoffman, who has made a series of over one hundred and fifty experiments after Mitscherlich's method, the reaction is not interfered with by the presence of either tartar emetic, magnesia, oxide of iron, musk, castor, opium, albumen, any of the metallic salts, volatile organic acids, nor by free acids; but it is interfered with or entirely prevented by iodine, calomel, and corrosive sublimate in large quantity, and metallic sulphides in the presence of free sulphuric acid, and particularly oil of wormseed. (*London Chem. News*, Jan. 1861, 50.) The same observer remarks that numerous experiments, by distilling the brain of various animals, blood, albumen, casein, fibrin, legumen, and other proteine compounds, with dilute sulphuric acid, failed to yield the least phosphorescence.

2. *Hydrogen Method.*

This method, first devised by L. Dusart and since improved by Fresenius, is based upon the property possessed by free phosphorus, and the lower oxides of phosphorus, of forming with nascent hydrogen phosphuretted hydrogen, which burns with a greenish flame. The color of the flame is not diminished in intensity by conducting the mixed gases over hydrate of potassium or caustic lime: these latter substances would retain any sulphuretted hydrogen present, which burns with a blue flame and thus interferes with the phosphorus reaction.

An ordinary gas-evolution flask is charged with pure diluted sulphuric acid and zinc, and the evolved hydrogen, after being conducted over pumice-stone moistened with a saturated solution of caustic potash, ignited as it escapes from a drawn-out tube provided

with a platinum burner. If the gas burns with a colorless flame, the phosphorus mixture is introduced by means of a funnel-tube into the flask, when the evolved gas will burn with a characteristic green color, which disappears if the tube becomes heated. For this reason the end of the tube should be surrounded with moistened cotton. If a piece of cold porcelain be depressed in the flame, the latter burns with an emerald-green color at the points of contact until the porcelain becomes heated.

On following this method, L. Dusart obtained from about the sixth of a grain of the paste of matches a flame that not only burned for an hour and a half with a visible green tint, but also produced on porcelain spots of a yellowish-red color, which resembled finely reduced phosphorus. (*Jour. de Chim. Méd.*, 1863, 663.) The evolved gas has a peculiar odor, and is luminous in the dark. The peculiar odor of hydrogen when obtained from iron and dilute acids, according to Dusart, is due to the presence of phosphuretted hydrogen.

The phosphide of silver yields by this method the same results as free phosphorus. The silver compound may be obtained by gently heating the phosphorus mixture, acidulated with sulphuric acid, for some hours in a flask through which a slow stream of carbonic acid gas is being passed, and collecting the evolved vapor in a solution of nitrate of silver. In this operation, the vaporized phosphorus passes through the atmosphere of carbonic acid without undergoing any change; but on coming in contact with the silver solution it gives rise to solid phosphide of silver and free phosphoric acid. The phosphide of silver is collected and washed on a filter, which has previously been washed in diluted nitric acid and water; it is then suspended in a little water and introduced into the hydrogen apparatus. The presence of phosphoric acid in the filtrate, separated from the silver compound, may be determined in the manner heretofore indicated.

Fresenius states that he obtained by this process the clearest evidence of the presence of phosphorus in a large quantity of putrid blood mixed with the composition scraped from the tip of a common lucifer-match, and this even in the presence of substances which prevent the luminosity of the phosphorus in experiments by Mitscherlich's method.

3. *Lipowitz's Method.*

This method is based upon the property possessed by sulphur when heated with free phosphorus of combining with it, even when present in very complex mixtures and in a highly comminuted state, and producing a compound in which the presence of the poison is readily determined. The phosphorus mixture, slightly acidulated with sulphuric acid, is gently boiled for about half an hour in a retort with a few small pieces of sulphur, the distillate being collected in an ordinary receiver.

The fragments of sulphur are then separated from the cooled mixture and washed with water. They will now emit the peculiar odor of phosphorus, and be luminous in the dark. When gently heated with strong nitric acid, they yield a solution containing phosphoric acid, together with more or less sulphuric acid. The presence of phosphoric acid in this mixture may be shown by evaporating the liquid to a small volume, diluting with a little water, filtering, neutralizing the filtrate with ammonia, and applying the magnesium test hereafter described.

The liquid that distils over into the receiver will usually contain one or more of the oxides of phosphorus, and have an alliaceous odor. When, however, only a minute quantity of phosphorus is present in the original mixture, the whole of it may be retained by the sulphur.

By this method, Lipowitz states that he detected phosphorus in complex organic mixtures containing only the 1–140,000th of their weight of the poison.

Since in medico-legal investigations for phosphorus it often becomes necessary to recover the poison, in part at least, as phosphoric acid, before describing the methods of separating the former from organic mixtures the general nature and chemical properties of the latter will be considered.

Phosphoric Acid.

General Chemical Nature.—Anhydrous phosphoric acid, or *phosphoric oxide*, is a compound of two atoms of phosphorus with five atoms of oxygen, P_2O_5; it is the highest oxide of phosphorus known. In its anhydrous state it forms a snow-white amorphous

mass, which has a strong affinity for water, and rapidly deliquesces when exposed to the air, forming a hydrate. Monohydrated phosphoric oxide is usually prepared by boiling phosphorus with diluted nitric acid, and evaporating the solution until, on cooling, it solidifies to a hard transparent mass; in this state it is known as *glacial phosphoric acid*, or *metaphosphoric acid*, and has the composition H_2O,P_2O_5, or HPO_3.

Phosphoric oxide also unites with two and with three molecules of water, forming respectively *pyrophosphoric acid*, $2H_2O$; P_2O_5, and *orthophosphoric acid*, $3H_2O$; P_2O_5. The last-mentioned is the ordinary phosphoric acid, and is usually represented by the formula H_3PO_4; thus: $3H_2O$; $P_2O_5 = 2H_3PO_4$.

Common phosphoric acid, or orthophosphoric acid, is capable of forming three series of salts, according as one, two, or all three of its atoms of hydrogen are replaced by a metal; it is therefore tribasic. The salts of this acid, except those of the alkalies, are insoluble in water; but they are freely soluble in the presence of a free acid, even in most instances of acetic acid.

Special Chemical Properties.—In the following investigations of the reactions of reagents with solutions of phosphoric acid, the latter was employed in the form of common phosphate of sodium. The fractions indicate the amount of *phosphoric oxide* in solution in one grain of water; the results, unless otherwise stated, refer to the behavior of one grain of the solution.

1. *Silver Nitrate.*

This reagent fails to produce a precipitate in solutions of free phosphoric acid; but in neutral solutions of the alkaline phosphates it occasions a light-yellow precipitate of tribasic phosphate of silver, Ag_3PO_4. The precipitate is readily soluble in ammonia, and also in nitric, acetic, and free phosphoric acids; hydrochloric acid changes it to white chloride of silver. From dilute solutions, the formation of the precipitate is much facilitated by the aid of a gentle heat.

1. $\frac{1}{100}$ grain of phosphoric oxide, in one grain of water, yields a copious yellow deposit, which remains amorphous.
2. $\frac{1}{1000}$ grain yields a very good precipitate.
3. $\frac{1}{10,000}$ grain: a very satisfactory deposit, of a very pale yellow color. The precipitate from ten grains of the solution has a very satisfactory yellow color.

4. $\frac{1}{50,000}$ grain: after a very little time, a quite distinct cloudiness appears. Ten grains of the solution yield a very satisfactory turbidity, but the yellow color is not apparent.

Nitrate of silver also throws down from neutral solutions of arsenious acid a yellow precipitate, which, however, usually becomes crystalline. The arsenical precipitate, like that from phosphoric acid, is readily soluble in ammonia and in free acids; but when dried, and heated in a reduction-tube, it yields a sublimate of octahedral crystals of arsenious oxide, in which it is readily distinguished from the phosphorus compound. The reagent produces yellowish-white precipitates in solutions of iodides and of bromides; but these precipitates are insoluble in dilute nitric acid, and only sparingly soluble in ammonia.

2. *Magnesium Sulphate.*

This reagent throws down from strong solutions of the alkaline *phosphates*, but not of free phosphoric acid, a white amorphous precipitate of phosphate of magnesium, $MgHPO_4$,Aq. The quantity of the precipitate is much increased by boiling the mixture, it then having the composition $Mg_3 2PO_4, 2\frac{1}{2}$Aq. One grain of a 1–100th solution of phosphoric oxide, in the form of an alkaline phosphate, yields a very good precipitate without the application of heat. Ten grains of the same solution yield, upon boiling the mixture, a very copious deposit. Ten grains of a 1–1000th solution remain clear on the addition of the reagent, but when the mixture is boiled it yields a quite good flocculent precipitate.

A *mixture* of magnesium sulphate, ammonium chloride, and free ammonia produces in solutions of free phosphoric acid and of alkaline phosphates a white crystalline precipitate of *ammonium magnesium phosphate*, NH_4MgPO_4,6Aq. This reaction is much more delicate and characteristic than that produced by magnesium sulphate alone. The formation of the precipitate from very dilute solutions is much facilitated by stirring the mixture with a glass rod. The precipitate is readily soluble in free acids, but insoluble in ammonia, even more so than in pure water.

1. $\frac{1}{100}$ grain of phosphoric oxide, when treated with the above mixture, yields a very copious, gelatinous precipitate, which in a little time becomes crystalline.
2. $\frac{1}{1000}$ grain: a copious precipitate, which immediately begins to

crystallize, and soon becomes entirely converted into feathery and stellate crystals, Plate IV., fig. 3.

3. $\frac{1}{5000}$ grain: an immediate crystalline precipitate, which soon becomes rather abundant.

4. $\frac{1}{10,000}$ grain yields an immediate cloudiness, and in a little time a crystalline deposit.

5. $\frac{1}{25,000}$ grain: in a very little time the mixture becomes turbid, and crystals can be seen by the microscope; after a few minutes there is a quite satisfactory crystalline deposit.

6. $\frac{1}{50,000}$ grain: after a few minutes crystals appear to the microscope, and after some minutes they are quite obvious to the naked eye.

7. $\frac{1}{100,000}$ grain: after about fifteen minutes crystals are perceptible to the naked eye.

This reagent mixture also produces a similar crystalline precipitate in solutions of arsenic acid. When, however, the arsenical precipitate is dissolved in just sufficient acetic acid, and the solution treated with nitrate of silver, it yields a reddish-brown deposit; whereas the phosphoric precipitate, when treated in the same manner, yields a white deposit. The same reddish-brown precipitate is produced by nitrate of silver from normal solutions of arsenic acid.

3. *Molybdate of Ammonium.*

The test-fluid is prepared by treating a solution of ammonium molybdate with sufficient nitric acid to redissolve any precipitate that first forms; or, according to Sonnenschein, who first proposed the test, one part of molybdic acid is dissolved in eight parts of ammonia solution, and this solution slowly added to twenty parts of nitric acid. Recently (1882), Kupfferschläger has advised to dissolve ten parts of molybdic acid in fifteen parts of aqua ammoniæ previously diluted with thirty parts of water, and add the solution little by little to one hundred parts of nitric acid of specific gravity 1.20. After a few days the clear liquid is decanted and ready for use.

To apply the test, a small quantity of the test-fluid is placed in a test-tube, and a few drops of the phosphoric acid solution added, when, if the reagent is greatly in excess, the mixture will acquire a yellow color and yield a yellow pulverulent precipitate of *ammonium phosphomolybdate.* From very dilute solutions of the acid the precipitate is slow to appear; the reaction is greatly promoted

by a gentle heat. According to M. Seligsohn, the precipitate contains only 3.14 per cent. of phosphoric oxide, its composition being $60MoO_3$; $4(3NH_4; PO_4)$; $15H_2O$: different formulæ, however, have been assigned to its composition.

In the presence of excess of the reagent, ammonium phosphomolybdate is insoluble in nitric, hydrochloric, and most other acids, even on boiling; but it is readily soluble in excess of free phosphoric acid and of alkaline phosphates, the caustic alkalies and their carbonates, and in the alkaline tartrates. (*Chem. Gaz.*, x., 1852, 216, 390.)

In examining the limit of the reaction of this test, one grain of the phosphoric acid solution was added to five fluid-grains of the test-fluid, placed in a small test-tube.

1. $\frac{1}{100}$ grain of phosphoric oxide produces an immediate yellow solution and a bright yellow precipitate, which in a little time becomes quite copious. The precipitate is much increased in quantity by warming the mixture.
2. $\frac{1}{1000}$ grain: the mixture immediately assumes a yellow color, and in a little time yields a copious yellow deposit. If the precipitate be dissolved in the mixture by excess of ammonia, and then a mixture of sulphate of magnesium and chloride of ammonium added, it yields an immediate crystalline precipitate of ammonium magnesium phosphate, not to be distinguished from that thrown down from a pure solution of phosphoric acid of the same strength.
3. $\frac{1}{10,000}$ grain: the mixture immediately assumes a yellow tint, which increases in intensity, and in a little time a yellow precipitate separates. Upon gently heating the mixture, it yields a good, yellow deposit.
4. $\frac{1}{50,000}$ grain: after a little time the mixture acquires a yellow tint; by heat the yellow color becomes very distinct, and yellow flakes separate. These gather upon the surface of the fluid and form an adherent, yellow pellicle.
5. $\frac{1}{100,000}$ grain: after several minutes, no perceptible change. But if the mixture be heated, it assumes a distinctly yellow color, and after a time small yellow flakes appear upon the surface of the liquid.

This reagent also produces a yellow coloration and precipitate in solutions of *arsenic* acid, but only, however, as first pointed out by

Sonnenschein, when the mixture is *heated* to about the boiling temperature. The absence of this acid may be shown by nitrate of silver, in the manner already indicated. So, also, on the application of heat, the reagent imparts a yellow color to solutions of *silicic acid;* but this substance yields no precipitate, nor does it even yield a yellow coloration, unless the mixture be heated.

Other Reactions.—Phosphoric acid is also precipitated, at least from neutral solutions, by acetate of lead, soluble salts of barium, strontium, calcium, and of several other metals. The lead precipitate is almost wholly insoluble in acetic acid, but most of the other precipitates are readily soluble in this acid. These reactions, however, are common to solutions of several other acids, and in most instances are much inferior in delicacy to the tests already mentioned.

Separation from Organic Mixtures.

The *odor* emitted by phosphorus is so peculiar that it will often serve to detect the poison with considerable certainty, even when present in very complex mixtures. It must be remembered, however, that the presence of other odors may entirely conceal that of this substance, especially if it is present only in minute quantity. We have even found this to be the case when comparatively large quantities of the poison were purposely added to animal mixtures which were undergoing decomposition. According to Dr. F. Hoffman (*Chem. News*, iii. 50), coffee, mustard, smoked meat, highly-seasoned food and beverages, and medicines containing odorous gum-resins, volatile oils, musk, castor, camphor, and chlorine, have the property of concealing the odor of the poison, at least if present only in minute quantity.

Organic mixtures containing free phosphorus, when exposed to the air, usually evolve vapors which are luminous in the dark, especially if the mixture be gently heated and stirred. If on thus examining the mixture any solid particles of the poison are found, they may be washed in water, then in alcohol, and preserved for future examination if necessary. If the mixture under examination is ammoniacal from putrefaction, before being examined in regard to its luminosity it should be acidulated with sulphuric acid. Should these means fail to prove the presence of the poison, the suspected mixture is examined by one or other of the following methods.

Mitscherlich's Method.—A comparatively large portion of the mixture, acidulated with sulphuric acid, may be examined after this method. As this is the most satisfactory process yet proposed for the detection of free phosphorus, it should never be omitted, unless the poison has already been discovered in its solid state. If during the distillation the contents of the flask become thick, they should be diluted with water, and the process continued as long as any luminosity appears in the condensing-tube. If the distillate thus obtained contains any globules of phosphorus, they are carefully separated from the liquid, then washed, dried between folds of bibulous paper, and weighed. The liquid may then, after the addition of a few drops of nitric acid, be concentrated to a small volume, and a portion of it examined by molybdate of ammonium for phosphoric acid; another portion may be neutralized with ammonia, and then treated with a mixture of magnesium sulphate and ammonium chloride, which will precipitate any phosphoric acid present as ammonium magnesium phosphate.

When this method yields a distinct luminosity or furnishes globules of phosphorus, it is certain that the poison was present in its free state. Should, however, the phosphorus have already undergone oxidation, this method will yield no evidence of its presence. Under these circumstances, the remaining contents of the flask are examined for oxides of phosphorus, in the manner described hereafter. It must also be borne in mind that the luminosity may be entirely prevented by the presence of certain volatile substances. These substances, however, would not prevent any free phosphorus present from passing over into the receiver, and there appearing at least in the form of an oxide. That the luminosity of phosphorus is not readily interfered with by the ordinary products of decomposition is shown by the following experiment.

The putrid mass resulting from exposing a human stomach with its contents, free from phosphorus, to the action of the air for six weeks, was made into a thin paste by the addition of water. Twenty-five hundred fluid-grains of this highly offensive mixture, acidulated with sulphuric acid, were then distilled with about the thirtieth of a grain of phosphorus, added in a finely divided state. Nearly as soon as the mixture reached the boiling temperature a very distinct phosphorescence appeared within the condenser, and continued without interruption for twenty-six minutes, when, the contents of

the flask having become very thick and black, the distillation was discontinued. The distillate thus obtained measured nearly eighteen hundred fluid-grains, had a milky appearance and very offensive odor, but no odor or globules of phosphorus were detected. When, however, this liquid was treated with a few drops of nitric acid, and evaporated to a small volume, then neutralized with ammonia, and treated with a mixture of magnesium sulphate and ammonium chloride, it gave a fine crystalline precipitate, which when further examined was found to represent very nearly the fiftieth of a grain of phosphorus.

Method of Lipowitz.—If in the application of this method the suspected mixture, after the addition of the fragments of sulphur, be boiled in a retort with a long neck, or the latter be connected with the receiver by means of a glass tube, and the operation performed in the dark, the vapors as they pass through the tube, if they contain phosphorus, will be phosphorescent, even, as we have in several instances found, when only a very small quantity of the poison is present. In this manner this process may, as it were, be combined with that of Mitscherlich. Yet, as the poison would thus be divided, part of it remaining in the retort with the sulphur and part passing over into the receiver, this method is advisable only in the absence of facilities for the application of Mitscherlich's method, in which the whole of the poison may be collected in the distillate.

Dusart's Method.—For the recovery of phosphorus from the contents of the stomach, intestines, and similar mixtures, the following method has been advised by L. Dusart. (*Jour. Chim. Méd.*, Sept. 1874, 400.) The mass, placed in a flask, is treated with a mixture of equal volumes of disulphide of carbon, ether, and alcohol in which has been previously dissolved one-half per cent. of sulphur, the ethereal mixture being added in sufficient quantity to form when well agitated an emulsion. In this operation any free phosphorus present will be dissolved by the disulphide of carbon mixture, and, uniting with the dissolved sulphur, form a compound of phosphorus and sulphur, much less readily oxidized than free phosphorus.

After standing twenty-four hours, the ethereal mixture is decanted, and the residue extracted a second and third time in the same manner. The mixed ethereal liquids are quickly filtered, in a covered funnel, into a retort, and then metallic copper recently reduced by hydrogen added portions at a time, until the last portions remain bright after

warming the mixture some minutes. After some hours, the mixture is heated on a water-bath until the ethereal liquid has distilled over; there will then remain in the retort a little water, fatty and extractive matters, and the copper covered with phosphorus and sulphur.

The coated copper is collected on a filter, washed with alcohol, then with ether; this process removes the fat, and leaves the copper compound as a black and brilliant substance, which is not sensibly acted upon by the air: it may be preserved in a dark flask for future examination. To show the presence of the phosphorus in the copper compound, the latter is placed in an apparatus in which pure hydrogen is being evolved and provided with a tube containing a caustic alkali, as heretofore described, when phosphoretted hydrogen will be evolved and burn with its characteristic green color.

Recovery as an Oxide of Phosphorus.—If the phosphorus has undergone oxidation, the method of Mitscherlich, as already stated, will fail to reveal its presence. But, if the poison has only passed to the state of phosphorous acid, it may still be detected by the *hydrogen method*, either directly by the flame reaction or after conversion into silver phosphide (*ante*, 205). Should it, however, have passed to the state of phosphoric acid, then this method will also fail.

Under these circumstances, the mixture, after the addition of water, and filtration if necessary, is treated with a few drops of nitric acid and concentrated to a small volume. It is then treated with slight excess of pure sodium carbonate, evaporated to dryness, and the residue slowly heated to fusion, by which the organic matter will be destroyed, while any phosphoric acid present will remain as sodium phosphate. The residue is then dissolved in a small quantity of water, and the solution examined by the usual tests for phosphoric acid. If, however, only a minute quantity of phosphoric acid be thus detected, this in itself will be no evidence that the phosphorus originally existed in its unoxidized state, since that acid in minute quantity is normally present in most organic mixtures.

Failure to detect the Poison.—In fatal poisoning by phosphorus, as by most other substances, the whole of it may be eliminated from the body previous to death, even when death takes place with the usual rapidity. Then, again, as this substance readily undergoes oxidation, it may thus, at least as free phosphorus, speedily disappear from the dead body. In Dr. Lewinsky's case, already cited, in which death occurred on the sixth day, a chemical examination of

the stomach and its contents, by Dr. Schauenstein, failed to yield any indication of the presence of phosphorus. So, also, in a case reported by Dr. Nitsche, in which a soldier purposely swallowed the ends of six ordinary packets of phosphorus-matches and died on the *fourth* day, a chemical examination of the stomach and a portion of the intestines, with their contents, two days after death, revealed no evidence of the presence of the poison. (*Amer. Jour. Med. Sci.*, Jan. 1858, 288.) Early in the history of this case a large quantity of the phosphorus mixture was expelled from the stomach by vomiting.

Cases are reported, however, in which this poison was detected after comparatively long periods. Thus, in a case quoted by Wharton and Stillé, it was detected in the contents of the intestines on the *tenth* day after it had been taken. And in a case reported by Dr. Ludwig, in which a child, three years and a half old, was poisoned by phosphorus-paste, about one grain of phosphorus in substance was obtained from the contents of the stomach and intestines, although the body had been buried *three weeks*. (*Jour. de Chim. Méd.*, 1863, 584.) This is the longest period we find recorded after which the poison has yet been detected in its free state in the human subject.

In some experiments upon guinea-pigs, each poisoned with twenty-three milligrammes (about one-third grain) of phosphorus, MM. Fischer and Müller (*Zeits. Anal. Chem.*, 1876, 57) found free phosphorus in the body at the end of eight weeks; in twelve weeks no free phosphorus, but phosphorous acid; and at the end of fifteen weeks only phosphoric acid.

Quantitative Analysis.—Any phosphorus found in its solid state, or obtained by Mitscherlich's method, may, of course, be weighed as such. When, however, the phosphorus has been converted into phosphoric acid, it may be determined as magnesium pyrophosphate, $Mg_2P_2O_7$. For this purpose the solution is treated with slight excess of a clear mixture of magnesium sulphate, ammonium chloride, and ammonia, and allowed to stand for several hours, in order that the precipitate may completely separate. The precipitate is then collected upon a filter, washed with water containing a little ammonia, dried, ignited, and, after cooling, weighed. Every one hundred parts of the ignited residue, if pure, correspond to sixty-four parts of phosphoric oxide, P_2O_5, or twenty-eight parts of free phosphorus.

CHAPTER IV.

ANTIMONY.

History.—Antimony is a bluish-white, hard, brittle metal, having a density of about 6.7: its symbol is Sb, and its atomic weight 122. When heated to near redness, it takes fire and burns with the evolution of dense white fumes of sesquioxide of antimony. The metal is unacted upon by cold sulphuric acid, but the hot acid converts it into an oxide with the evolution of sulphurous oxide gas. Hot concentrated nitric acid oxidizes it chiefly into antimonic acid; hydrochloric acid, even at the boiling temperature, has little action upon it, but it is readily soluble in nitro-muriatic acid.

Antimony forms two principal oxides: *trioxide*, or *sesquioxide* of antimony, known also as *antimonious oxide*, Sb_2O_3, and *pentoxide*, or *antimonic oxide*, Sb_2O_5; the first of these oxides is basic, the other acid, in properties. With sulphur the metal forms two sulphides, corresponding in composition with the oxides named. Antimony also unites in two proportions with chlorine, forming *trichloride*, or *antimonious chloride*, $SbCl_3$, and *pentichloride*, or *antimonic chloride*, $SbCl_5$.

When taken in its pure state into the system, antimony seems to be inert. But several of its preparations are more or less poisonous. The only one of these, however, likely to become the subject of a medico-legal investigation is *tartar emetic*.

Tartar Emetic.

Composition.—This substance, known also as tartarized antimony or tartrate of antimony and potassium, is a compound of potassium, oxide of antimony, and tartaric acid, with water of crystallization, its formula being $2KSbOC_4H_4O_6$; H_2O; molecular weight 668. It is prepared by the action of antimonious oxide upon the acid tartrate

of potassium, or *cream of tartar;* thus: $2KHC_4H_4O_6 + Sb_2O_3 = 2KSbOC_4H_4O_6; H_2O$. Antimonious oxide, in its free state, is a white crystallizable substance, which is insoluble in water, and only sparingly soluble in nitric acid, but readily soluble in hydrochloric and tartaric acids, and in the caustic alkalies. The poisonous effects of tartar emetic are entirely due to the presence of the antimonious oxide.

Symptoms.—As a summary of the symptoms usually produced by tartar emetic, when swallowed in large quantity, may be mentioned the following: nausea, violent and continuous vomiting, burning pain in the stomach and bowels, profuse purging, great thirst, violent cramps, small and feeble pulse, coldness of the extremities, great prostration, and in some instances convulsions and delirium. The matters discharged from the bowels are usually very fluid, and frequently contain bile. The urine is generally increased in quantity, and its passage sometimes attended with pain. It is a remarkable fact that in several of the reported instances of poisoning by this substance there was neither vomiting nor purging; in these, however, the other symptoms were present in an aggravated form.

A man of strong constitution, aged fifty years, for the purpose of self-destruction, swallowed about thirty-seven grains of tartar emetic. Violent vomiting, excessive purging, and convulsions soon ensued. On the morning of the third day, he complained of violent pain in the epigastrium, which was much distended; he spoke with difficulty, and appeared as if intoxicated; the pulse was imperceptible. During the day the bowels became tympanitic and more painful, and delirium supervened. The next morning all the symptoms were aggravated, and in the evening the delirium became furious; convulsions then set in, and death occurred during the night, nearly four days after the poison had been taken. (*Orfila's Toxicologie*, 1852, i. 623.)

The following remarkable case of recovery is reported by Dr. J. T. Gleaves. (*Western Jour. of Med. and Surg.*, Jan. 1848, 23.) A young man of strong constitution swallowed a tablespoonful of tartar emetic (about an ounce). In an *hour and a half* afterward, although he drank freely of warm water and repeatedly tickled his fauces with his finger, no vomiting had occurred. During the first three hours he vomited only two or three times, and the matter ejected was chiefly the warm water taken to induce vomiting. Two

hours after taking the poison there was violent involuntary purging, and he became pulseless, speechless, and was apparently dying. Three hours after the occurrence, when the case was first seen by Dr. Gleaves, the breathing was slow and difficult, the face pale, features shrunken, eyes fixed, pupils dilated, and the surface cold; there was no pulse, and the patient was apparently unconscious. In seven hours the purging ceased, consciousness returned, and there was great thirst, and a sense of burning pain in the throat, œsophagus, stomach, and bowels. Great irritability of the stomach ensued, and the matters vomited were tinged with blood. On the evening of the following day, the patient was again pulseless and speechless, and the abdomen was tympanitic and painful to the touch. The vomiting continued, but the purging was arrested. On the third day, there was occasional vomiting, and the throat was sore and covered with pustules; there was also painful micturition, the urine being copious and highly colored. On the fourth day, the whole body was covered with genuine tartar emetic pustules. After a few days these began to heal, and in about two weeks the patient was perfectly well.

Period when Fatal.—A child, recovering from measles, died in *an hour* from the depressing effects of three-quarters of a grain of tartar emetic, prescribed as a medicine. (*Jour. de Chim.*, 1847, 472.) In a case reported by Dr. C. Ellis, an unknown quantity of the poison proved fatal to a young lady, aged twenty-one years, in *seven hours*. The symptoms were violent vomiting and purging, accompanied with a sense of burning in the mouth, dryness of the throat, and great thirst. Death took place apparently from exhaustion, without convulsions or any cerebral symptoms. (*Boston Med. and Surg. Jour.*, Dec. 1856, 400.) In a case reported by Dr. Pollock, in which sixty grains of tartar emetic had been taken, death occurred in *ten hours*. (*London Med. Gaz.*, May, 1850, 801.) In this instance, the patient, a robust, healthy man, aged about thirty years, was very soon seized with violent vomiting and retching. In two hours after the poison had been taken, there was still violent retching at short intervals, and the man complained of heat and constriction in the throat, and pain in the epigastrium; the respiration was frequent; the skin covered with perspiration; the pulse rapid and small. In a few hours afterward the vomiting ceased, and the patient became insensible; the respiration was slow and labored, but not stertorous; pulse very rapid and almost imperceptible; and the power of swal-

lowing had ceased. Death took place tranquilly, and without convulsions.

The cases now cited are among the most rapidly fatal yet reported. Instances are recorded in which death did not occur until after the lapse of several days; and Dr. Deutsch relates a case in which a woman, who took by mistake a scruple of tartar emetic, was brought exceedingly low by its violent action, and died in the course of a year in consequence of its irritant effects upon the intestinal canal. (Wharton and Stillé, *Med. Jur.*, 553.)

Fatal Quantity.—Several instances are on record in which very small doses of tartar emetic produced most violent symptoms. Thus, in an instance related by Dr. A. Stillé (*Mat. Med.*, ii. 346), a dose of not more than *half a grain* produced violent vomiting and purging, and a state closely resembling the collapse of cholera. The patient was an insane female, whose general health, however, was perfect. Of thirty-seven cases of acute poisoning by tartar emetic collected by Dr. Taylor, sixteen proved fatal. Of the fatal cases, the smallest dose was in a child, *three-quarters of a grain*, and in an adult, *two grains;* but in the latter case there were circumstances which favored the fatal operation of the poison. (*Guy's Hosp. Rep.*, 1857, 415.) Mr. Hartley relates two instances in which ten grains each proved fatal to two children, aged three and five years respectively. In a case related by Dr. C. A. Lee, a child a few weeks old, who swallowed about fifteen grains of the salt in solution, was seized with violent vomiting and purging, attended with convulsions, which soon proved fatal. (*New York Med. and Phys. Jour.*, xxx. 302.) Two cases have already been cited in which thirty-seven grains and sixty grains respectively proved fatal to healthy adults.

The following remarkable case of recovery is related by Dr. McCreery. A physician swallowed half an ounce of tartar emetic, put up by mistake for Rochelle salt. In about thirty-five or forty minutes after taking the poison he experienced some nausea, which in about five minutes more was succeeded by vomiting. Copious draughts of green tea and large doses of tannin were then administered; and these were followed by the exhibition of albumen and an infusion of flaxseed. But the vomiting, which was very distressing, continued, with little intermission, for several hours. There was also very severe purging, with most violent cramps of the legs, and slighter ones of the wrists. The first evacuation from the bowels

was purely serous; those which followed were of a bilious character, but very loose: there were no cramps of the stomach. These symptoms gradually subsided, and after several days the patient was quite well. (*Amer. Jour. Med. Sci.*, Jan. 1853, 131.) In a case communicated to me by Dr. R. Denig, a woman recovered in a few days after taking fully sixty grains of the salt in solution. Within ten minutes after taking the dose the patient experienced great distress and burning pain in the stomach, accompanied by retching and vomiting. A case is recently reported in which recovery took place after one hundred and seventy grains of the salt had been taken. (*Med. Rec.*, New York, 1883, 401.) It is well known that in certain inflammatory diseases tartar emetic may be administered in very large doses without producing any of its ordinary effects.

TREATMENT.—If there is not already free vomiting, it should be promoted by the administration of large draughts of warm water; or the stomach may be emptied by means of the stomach-pump. As a chemical antidote, various vegetable astringents, such as a strong infusion of Peruvian bark, green tea, nut-galls, or oak bark, have been highly recommended; and instances are reported in which their exhibition was apparently attended with very great advantage. It has, however, been denied that these substances serve to neutralize the poison.

After the poison has been expelled from the stomach, opium may be administered to check the excessive vomiting. For this purpose a strong decoction of coffee has also been highly recommended.

POST-MORTEM APPEARANCES.—In the case cited from Orfila, which proved fatal in about four days, the mucous membrane of the stomach, except near the gullet, where it was healthy, was red, tumefied, and covered with a viscid coating, which was easily separated; the duodenum was in a similar condition, but the other intestines were healthy. The intestines were entirely empty. The brain was congested and softened. The organs of the chest were healthy.

In the case related by Dr. Lee, in which fifteen grains of the poison had been taken, the mucous membrane of the stomach was red and softened, and on holding it up to the light it appeared of a bright crimson color. The stomach contained a small quantity of slimy mucus, and, like the mucous membrane, was softened. The texture of the cardiac orifice seemed more changed than that of the

pyloric. The duodenum was of a deep brown color, almost livid, and contained the same kind of substance as found in the stomach. The inflammation extended no farther than the colon. The vessels of the scalp, as well as those of the brain, and the right side of the heart, were distended with blood. The ventricles of the brain were half filled with fluid, and there was effusion between the pia mater and the arachnoid membranes.

In Dr. Ellis's case, thirty-nine hours after death, the body was quite rigid, and there was considerable bluish discoloration about the back of the neck and the hands. The stomach contained a quantity of gruel-like, acid liquid, in which a considerable quantity of antimony was found. No well-marked morbid appearances were detected in any of the abdominal organs. The brain was not examined.

Chemical Properties.

General Chemical Nature.—Tartar emetic, as found in the shops, is usually in the form of a white amorphous powder. In its pure state it crystallizes in large, transparent, odorless octahedrons having a rhombic base. The crystals are slightly efflorescent at ordinary temperatures, and when heated to 100° C. (212° F.) become anhydrous.

When heated in a reduction-tube, by the flame of a spirit-lamp, tartar emetic readily blackens, from the decomposition of the organic acid, and is soon reduced to a mixture of charcoal and metallic antimony. It undergoes a similar change when heated upon platinum-foil, quickly destroying the platinum in contact with the heated mass. Heated on charcoal before the blow-pipe flame, the charred mass burns with the production of a widely diffused incrustation, the thicker portions of which have a whitish color, while the thinner ones have a bluish appearance; at the same time it yields globules of metallic antimony, which boil and are slowly dissipated by the continued action of the heat. If the globules are allowed to cool, they will be found exceedingly brittle.

According to R. Brandes, tartarized antimony is soluble in from twelve to fourteen parts of water at the ordinary temperature, and in less than three parts of boiling water. From a warm saturated solution the salt separates on cooling in beautiful bold crystals, Plate IV., fig. 4. The same crystals separate when one grain of a 1–1000th or stronger solution of the salt is allowed to evaporate

spontaneously to dryness; from more dilute solutions the residue is usually destitute of any well-defined crystals. Aqueous solutions of tartar emetic are colorless, have a nauseous, metallic taste, and a feeble acid reaction, even when the liquid contains only the 1–1000th of its weight of the salt. These solutions after a time undergo decomposition, the organic acid giving rise to a filamentous growth: we have found this formation make its appearance, after several days, in solutions containing even less than the 1–50,000th of their weight of the antimony compound.

Tartar emetic is insoluble in alcohol. If this liquid be added to an aqueous solution of tartar emetic containing even something less than the 1–100th of its weight of the salt, the latter is precipitated in the form of plumose crystals; sometimes, however, the precipitate also contains octahedral crystals.

Special Chemical Properties.—When tartar emetic in its solid state is moistened with a solution of sulphide of ammonium or of sulphuretted hydrogen, it immediately acquires an orange-red color, due to the production of a sulphide of antimony. This reaction is peculiar to antimony, and will manifest itself with the least visible quantity of the salt. Even the residue left on evaporating one grain of liquid containing only the 1–10,000th of a grain of the pure salt will yield a very satisfactory coloration.

In the following investigations in regard to the special reactions of reagents with *solutions* of tartar emetic, pure aqueous solutions of the salt were employed. The fractions employed indicate the amount of *sesquioxide of antimony*, Sb_2O_3, present in *one grain* of the solution. The amount of crystallized tartar emetic represented in these cases may be readily obtained by multiplying the fractions by 2.28.

1. *Sulphuretted Hydrogen.*

From somewhat strong *normal* solutions of tartar emetic this reagent throws down a deep orange-red precipitate of *sesquisulphide of antimony*, or *antimonious sulphide*, Sb_2S_3; in more dilute solutions it produces an orange-red turbidity, but no precipitate, at least for several hours. The formation of the precipitate from dilute solutions is much facilitated by heat. From solutions acidulated with hydrochloric acid, however, even when very dilute, the reagent produces an immediate precipitate.

The precipitate is insoluble in *diluted* hydrochloric acid, but

soluble in the *concentrated* acid, even at ordinary temperatures, and still more readily under the action of heat, with the formation of trichloride of antimony and the evolution of sulphuretted hydrogen gas. Fuming nitric acid converts it into a white insoluble compound of antimony. It is readily soluble in the fixed caustic alkalies, but insoluble in ammonia: at least we find that when one part of the moist precipitate is frequently agitated for some days with 10,000 parts of ammonia solution it does not entirely disappear, and that one part with even 25,000 parts of ammonia requires some hours for solution. When dried and fused with sodium nitrate, it gives rise to sodium metantimoniate and sulphate.

In the following examination in regard to the limit of this test, *five grains* of the antimony solution, placed in a small test-tube, were acidulated with hydrochloric acid, and then treated with the reagent.

1. 1–100th solution of sesquioxide of antimony ($=\frac{1}{20}$ grain Sb_2O_3) yields a very copious, light orange-red precipitate. Solutions of tartar emetic as strong as this require about half their volume of hydrochloric acid to redissolve the precipitate first produced by the acid. When tartaric acid is employed as the acidifying agent, the precipitate produced by the sulphur reagent has a much deeper red color than when produced in the presence of hydrochloric acid.
2. 1–1000th solution: an immediate precipitate, which very soon becomes quite abundant. A *normal* solution of tartarized antimony of this strength yields with the reagent a deep orange solution, but no precipitate, even after standing twenty-four hours.
3. 1–10,000th solution: an immediate turbidity, and, after a little time, a good deposit. If the mixture be warmed, the precipitate separates almost immediately. When the solution is acidulated with tartaric acid, the precipitate requires several hours for its separation.
4. 1–25,000th solution: in a very little time the mixture acquires an orange tint; and after several hours there is a satisfactory deposit.
5. 1–50,000th solution: in a little time the liquid assumes a yellow tint, then a reddish hue, and after several hours yields a quite perceptible orange-yellow deposit.
6. 1–100,000th solution: after some minutes the liquid acquires a

faint yellow tint, but undergoes no further change for at least several hours.

The reaction of this reagent, as already intimated, is quite characteristic of antimony. If the precipitate be dissolved in hot hydrochloric acid, and the solution after cooling treated with several times its volume of water, it yields a white precipitate, consisting of sesquioxide and trichloride of antimony, which after a time becomes crystalline, and is readily soluble in tartaric acid.

Sulphide of Ammonium, also, throws down from comparatively strong normal solutions of tartar emetic a precipitate of sesquisulphide of antimony, which is soluble in excess of the reagent. In five grains of a 1–1000th solution of sesquioxide of antimony the reagent produces a good yellow-orange deposit. In more dilute solutions it fails to produce a precipitate, but communicates to the liquid an orange or yellowish-red color. In the presence of a free acid, however, it precipitates even highly dilute solutions of the salt.

2. *Acetate of Lead.*

This reagent produces in normal solutions of tartar emetic a white amorphous precipitate of the double tartrate of antimony and lead, $Pb(SbO)_2C_8H_8O_{12}$, which is readily soluble in acetic and tartaric acids, and decomposed by nitric acid with the production of a white flocculent deposit.

1. $\frac{1}{100}$ grain of sesquioxide of antimony, as tartar emetic, in one grain of water, yields a very copious precipitate.
2. $\frac{1}{1000}$ grain: a very good flocculent precipitate.
3. $\frac{1}{10,000}$ grain yields a very satisfactory deposit.
4. $\frac{1}{25,000}$ grain: after a little time the mixture becomes quite turbid.

Acetate of lead also produces white precipitates in solutions of various other substances. But the antimony deposit differs from all these in that when washed and moistened with sulphide of ammonium it immediately assumes an orange-red color; after a little time, however, this color changes to a dark brown or nearly black hue.

3. *Metallic Zinc.*

When a drop of a solution of tartar emetic is placed on a piece of platinum-foil and acidulated with a small drop of hydrochloric acid, the addition of a fragment of zinc causes the separation of

metallic antimony, which adheres to the *platinum* covered by the liquid, forming a black or brownish stain (Fresenius). The deposit is readily soluble in nitric acid, especially if warmed, but only sparingly soluble in concentrated hydrochloric acid; when washed and dried, it is easily dissipated by heat.

1. $\frac{1}{100}$ grain of sesquioxide of antimony, in solution in one grain of water, when treated in the above manner, yields a very copious, deep black deposit.
2. $\frac{1}{1000}$ grain: a very good deposit.
3. $\frac{1}{5000}$ grain: after a very little time there is a very satisfactory dark-brown stain.
4. $\frac{1}{10,000}$ grain: after a few minutes a very distinct brownish stain makes its appearance.

The antimonial nature of these deposits may be shown by moistening the washed stain with nitric acid, and evaporating to dryness at a gentle heat, when the residue, on being touched with sulphide of ammonium, will assume an orange-red color.

Under the action of this test solutions of *arsenic* yield no deposit; whilst solutions of *tin* yield a deposit upon the *zinc*, but none upon the platinum.

4. *Metallic Copper.*

When a solution of tartar emetic is acidulated with hydrochloric acid, and boiled with a slip of bright copper-foil, the antimony compound undergoes decomposition with the deposition of *metallic antimony* upon the copper, in the form of a violet or gray coating, the color depending upon the thickness of the deposit. It is obvious that the thickness of the deposit produced by a given quantity of the metal will depend upon the size of the copper-foil employed in the experiment.

When one grain of the tartar emetic solution, placed in a thin watch-glass, is acidulated and heated with a very minute portion of the foil, it yields as follows:

1. $\frac{1}{100}$ grain of sesquioxide of antimony: the copper immediately assumes a violet color, and soon receives a thick, dark-gray coating.
2. $\frac{1}{1000}$ grain yields much the same results as 1.
3. $\frac{1}{10,000}$ grain: in a little time the copper presents a beautiful violet color.

4. $\frac{1}{50,000}$ grain yields a very distinct reaction.
5. $\frac{1}{100,000}$ grain: when the liquid is evaporated to near dryness, the copper acquires a perceptible violet tarnish.

The production of a metallic deposit upon copper under the above conditions is common to antimony, arsenic, mercury, and some few other metals. The violet color of the antimony deposit is rather peculiar; but the deposit from this metal does not always present this color, and, moreover, very thin deposits of arsenic may present a similar hue. When the coated copper is washed, dried, and heated in a narrow reduction-tube, the *antimony* deposit, if not in too minute quantity, yields a sublimate which forms quite near the heated slip of copper, and is generally amorphous, or at most granular, in form, but it *may* contain well-defined *octahedral* crystals of antimonic oxide, and sometimes crystalline needles. The *arsenic* deposit under like conditions is vaporized at a lower temperature, and yields, under proper conditions, a sublimate fully half an inch above the copper, and consisting wholly of octahedral crystals. The sublimate from mercury appears in the form of minute metallic globules. The other metals referred to fail to yield a sublimate when thus treated.

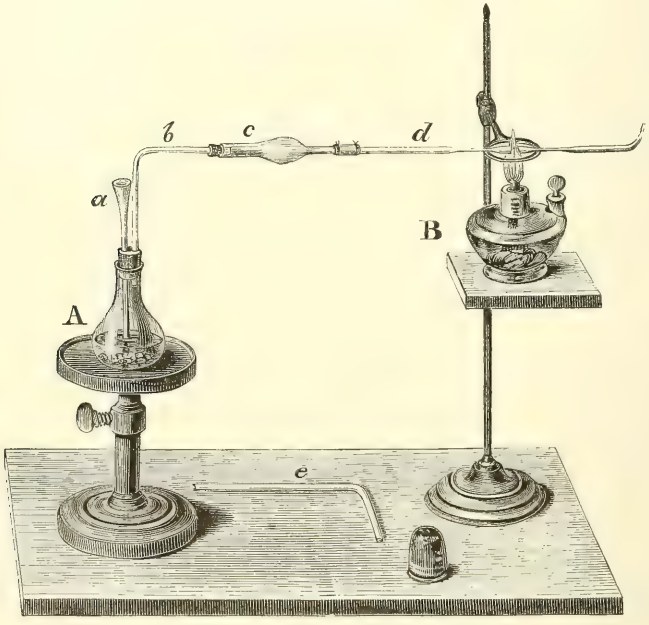
The true nature of the antimony deposit may be shown, as first advised by Mr. Watson, by boiling the coated copper in a dilute solution of caustic potash, the coated metal being occasionally withdrawn from the liquid and exposed to the air to favor the oxidation of the antimony, when, after a time, the deposit will be entirely dissolved as antimoniate of potassium. On now removing the copper-foil, and acidulating the liquid with hydrochloric acid, concentrating to a small volume, and then treating it with sulphuretted hydrogen gas, pentasulphide of antimony, Sb_2S_5, of an orange-red color, will be precipitated. This method will serve to identify even very small deposits of the metal.

5. *Antimonuretted Hydrogen.*

When a solution of tartar emetic, or of any of the soluble salts of antimony, is mixed with zinc and sulphuric acid, in the proportion to evolve hydrogen, the salt is decomposed and the antimony evolved as antimonuretted hydrogen gas, SbH_3. This decomposition may be effected in the apparatus of Marsh, first devised for the detection of arsenic, Fig. 3.

Pure zinc and sulphuric acid, previously diluted with about four volumes of water, are placed in the flask A, which is furnished with a drying-tube, *c*, and a reduction-tube, *d*, the latter of which is of hard glass and made to terminate in a drawn-out point. The drying-tube should be loosely filled with fragments of calcium chloride. When only a minute quantity of antimony solution is to be examined, the glass flask may be replaced by a test-tube. After the apparatus has become completely filled with hydrogen, a small quantity of the an-

FIG. 3.



Apparatus for the detection of antimony.

timony solution is introduced into the flask by means of the funnel-tube *a*, when in a few moments the evolved gas will contain antimonuretted hydrogen, the presence of which may be shown by three different methods.

1. If the gas as it escapes from the end of the reduction-tube be ignited, it burns with a bluish flame, and, unless the amount of antimony present is very minute, evolves white fumes of sesquioxide of antimony. If these fumes be received upon a cold surface, as a piece of porcelain, they yield a white amorphous deposit, which

immediately acquires an orange-red color when moistened with sulphide of ammonium. If a piece of cold porcelain, held in a horizontal position, be brought in contact with the flame, the antimony will condense in the form of a black, nearly circular spot or stain, which is usually surrounded by a grayish ring; as soon as a spot has thus formed, the flame should be received upon a fresh portion of the porcelain.

If the experiment be performed in a small apparatus, fifty grains of a fluid mixture containing the 1–10,000th of its weight of sesquioxide of antimony ($=\frac{1}{200}$ grain Sb_2O_3) will yield quite a number of spots of the metal.

Antimony and arsenic are the only metals that under the above conditions will yield metallic spots upon a cold surface. The spots from these two metals generally differ somewhat in regard to their physical appearance, those from antimony being usually dull, whereas those from arsenic have generally a bright metallic lustre. They differ greatly, however, in regard to some of their other properties. Thus, the antimony-stains are slowly and with difficulty dissipated by the flame of a spirit-lamp, whilst those from arsenic are readily volatilized. Again, the antimony spots readily dissolve in yellow sulphide of ammonium, and the solution, even from very small stains, when gently evaporated to dryness, leaves a red or orange-red residue of sulphide of antimony, which is soluble in strong hydrochloric acid, but insoluble in ammonia; whereas the arsenic-stains dissolve but slowly in yellow sulphide of ammonium, and the solution leaves upon evaporation a yellow residue of arsenious sulphide, insoluble in hydrochloric acid, but readily soluble in ammonia. Moreover, the antimony-stains are insoluble or dissolve with great difficulty in a solution of sodium or calcium hypochlorite, whilst the arsenic spots readily disappear when touched with a solution of this kind.

2. When a portion of the reduction-tube is heated to redness, the antimonuretted hydrogen passing through the tube is decomposed with separation of metallic antimony, which, when only in small quantity, is deposited within the tube wholly on the *inner* side of the part to which the flame is directly applied, but when in larger quantity, on both sides of the flame. Arsenic under like circumstances yields a somewhat similar deposit; but in this case the whole of the metal is deposited in the tube on the *outer* side of the part to which the flame is applied.

A much smaller quantity of antimony will in this manner furnish a deposit that will produce spots from the ignited jet upon porcelain. *Fifty grains* of a solution containing the 1–50,000th of its weight of sesquioxide of antimony ($= \frac{1}{1000}$ grain Sb_2O_3), when treated in a small apparatus, will yield a very good brownish-black deposit; and a similar quantity of a 1–500,000th solution, a very distinct brownish stain, within the heated tube. Deposits of the metal produced by this method exhibit the same chemical reactions as those produced on porcelain by the ignited gas.

3. If the antimonuretted hydrogen be conducted into a solution of silver nitrate, the whole of the antimony is precipitated as antimonide of silver, Ag_3Sb, in the form of a black powder. The chemical reaction in this case is as follows: $SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3$. When only a minute trace of antimony is present, the whole of the precipitate collects in the lower end of the delivery-tube, in the form of a black ring.

This reaction is extremely delicate, and the method can be applied with a much smaller quantity of fluid than either of those just mentioned. When the operation is performed in a small test-tube and the evolved gas conducted into a few drops of the silver-solution, five fluid-grains of a 1–10,000th solution of the antimony oxide will produce a quite large, black deposit, much of which remains in the end of the delivery-tube. A similar quantity of a 1–50,000th solution produces after several minutes a very satisfactory deposit; and a 1–100,000th solution will produce in about fifteen minutes a very distinct reaction.

Solutions of arsenic, of sulphides, and of several other substances will also under similar conditions evolve gaseous compounds, which produce black precipitates in a solution of silver nitrate. In the action of the arsenical compound, the precipitate consists alone of metallic silver, the arsenic being oxidized into arsenious oxide, which remains in solution.

The true nature of the antimony precipitate, or antimonide of silver, may be shown by collecting the deposit on a filter, washing with warm water, and boiling with dilute hydrochloric acid, in which the antimony will dissolve, while the silver will remain in an insoluble form. If the quantity of precipitate present is too minute to be separated from the filter, the portion of the latter containing the deposit is boiled in the dilute hydrochloric acid. When the

acid mixture has cooled and the deposit completely subsided, it is transferred to a filter which has previously been moistened with water, and the filtration repeated if necessary until the filtrate is perfectly clear. On now treating the solution with sulphuretted hydrogen, sesquisulphide of antimony, of its peculiar color, will be thrown down.

Professor Hofmann has recommended to boil the washed antimonide of silver with a solution of tartaric acid, in which the antimony readily dissolves, while the silver remains unchanged; the solution is then filtered and treated with sulphuretted hydrogen. (*Quart. Jour. Chem. Soc.*, April, 1860, 79.) By either of the methods now considered, an exceedingly minute quantity of antimony may be recovered from the silver precipitate.

From what has already been stated, it is obvious that the method under consideration will serve to detect antimony in the presence of arsenic, and the latter in the presence of the former. And this may be effected even when the metals are present in very minute and disproportionate quantities.

Antimonuretted hydrogen is also decomposed by an alcoholic solution of potassium hydrate, with the production of a black precipitate. Arsenic under similar conditions fails to produce a precipitate.

Other Reactions of Tartar Emetic.—*Nitric acid* produces in somewhat strong solutions of tartar emetic a white amorphous precipitate, which, according to Geiger, consists of a basic nitrate of antimonic oxide. The precipitate is soluble only in very large excess of the acid, but is readily soluble in tartaric acid; in solutions containing free tartaric acid, therefore, the reagent fails to produce a precipitate. When the washed precipitate is touched with sulphide of ammonium, it immediately assumes an orange-red color. One grain of a 1–100th solution of sesquioxide of antimony when treated with a drop of the acid yields a quite copious deposit, which does not disappear on the further addition of several drops of the reagent. One grain of a 1–100th solution yields with a small drop of the acid a very fair precipitate.

Hydrochloric acid occasions in concentrated solutions of the salt a white precipitate, which is much more readily soluble in excess of the reagent than in the preceding reaction; it is also very readily

soluble in tartaric acid. One grain of a 1–100th solution of sesquioxide of antimony yields with a drop of the reagent a quite good precipitate, which disappears when the mixture is stirred. This acid also produces white precipitates in solutions of silver, of lead, and of mercurous combinations. The silver precipitate is readily soluble in ammonia, and that from mercury is turned black, whilst the precipitates from lead and antimony are unchanged by this reagent. Sulphide of ammonium causes the antimony precipitate to assume an orange-red color, whilst it turns the lead-deposit black. The antimony precipitate is the only one of these that is soluble in tartaric acid.

Sulphuric acid throws down from similar solutions a white amorphous precipitate, which becomes orange-red when touched with sulphide of ammonium. The production of a white precipitate by this acid is common to solutions of several other metals.

Ammonia precipitates from solutions of tartar emetic white sesquioxide of antimony, which is insoluble in excess of the precipitant. One grain of a 1–100th solution of the antimony oxide yields a very good precipitate; and a similar quantity of a 1–1000th solution yields a quite fair, granular deposit, especially if the mixture be stirred. Ammonium carbonate fails to produce a precipitate even in concentrated solutions of the antimonial compound.

Potassium and Sodium hydrates produce in quite concentrated solutions of the salt white amorphous precipitates, which are readily soluble in excess of either reagent. The carbonates of these alkalies, however, throw down white precipitates that are insoluble in excess of the precipitant; the limit of these reactions is about the same as that of ammonia.

When a solution of tartar emetic is treated with sufficient excess of potassium hydrate to redissolve the precipitate first produced, and a solution of *silver nitrate* then added, it produces a brownish-black precipitate, consisting of a mixture of suboxide and monoxide of silver, while the antimony remains in solution as potassium antimoniate. If the precipitate thus produced be treated with ammonia, the monoxide of silver is dissolved, while the suboxide remains as a dense black powder. One grain of a 1–10,000th solution of antimony sesquioxide, when treated after this method, will yield a very satisfactory black deposit; and the reaction is visible when a similar quantity of even a 1–25,000th solution of the antimony compound

is employed. Nitrate of silver alone produces in solutions of the antimony salt a white precipitate.

Corrosive sublimate slowly throws down from solutions of the salt, even when quite dilute, a white flocculent precipitate. *Chromate* and *dichromate of potassium* impart to very strong solutions a greenish color, and throw down a slight, greenish precipitate. *Ferro-* and *ferri-cyanide of potassium* fail to produce a precipitate even in concentrated solutions of the antimony compound.

Separation from Organic Mixtures.

Suspected Solutions.—The same method of analysis is equally applicable for the examination of suspected articles of food or drink, vomited matters, and the contents of the stomach. The mixture, after the addition of water if necessary, is acidulated with hydrochloric acid, a little tartaric acid added, and the whole exposed to a gentle heat for about fifteen minutes. When the mixture has cooled, it is thrown upon a muslin strainer, the strained liquid filtered, and the filtrate, after concentration if necessary, exposed to a current of sulphuretted hydrogen gas as long as a precipitate is produced, and then allowed to stand in a moderately warm place for several hours, in order that the precipitate may completely subside.

If antimony is present in comparatively large quantity, the precipitate thus obtained will have a more or less orange-red color; if, however, the metal is present in only minute quantity, or the deposit contains much organic matter, it will present a yellow or brownish appearance. The precipitate is now collected upon a filter, washed with water containing a little hydrochloric acid, and then heated with strong hydrochloric acid, when any sesquisulphide of antimony present will be decomposed and the metal dissolved as trichloride. After solution has taken place, the heat should be continued until the odor of the sulphuretted hydrogen, evolved by the decomposition, has entirely disappeared.

A small portion of the clear liquid may now be examined by the *zinc* and *copper tests* in the manner already described, except that it is not necessary to add hydrochloric acid, since this is already present. Another portion of the liquid may be treated with large excess of water, when the antimony, unless present in only very minute quantity, will be precipitated as white oxychloride ($5Sb_2O_3$; $2SbCl_3$), the

true nature of which is fully established by its assuming an orange-red color when moistened with sulphide of ammonium, as well as by its ready solubility in tartaric acid. Should these tests yield positive reactions, a given portion of the solution, properly diluted, may be treated with sulphuretted hydrogen gas, and from the amount of antimony sesquisulphide obtained, the quantity of tartar emetic determined in the manner hereafter described.

If it is desired to reconvert the antimony present in the hydrochloric acid solution into tartar emetic, it may be precipitated, by addition of water, as oxychloride, and the precipitate collected, washed, and then agitated for some time with a very dilute solution of sodium carbonate. In this operation the oxychloride of antimony will be entirely converted into sesquioxide of the metal, the chlorine being taken up as chloride of sodium: care should be taken to employ only a very dilute solution of the sodium salt, since otherwise more or less of the antimony compound might be dissolved. The precipitate is now collected, washed, and digested at a moderate heat with a little water containing an appropriate quantity of potassium tartrate, or *cream of tartar*, when it will be dissolved as tartar emetic, the presence of which may be determined by the usual tests.

Should the precipitate produced from the original solution by sulphuretted hydrogen have a dark color, it should not be concluded, from this circumstance alone, that the metal is entirely absent; since it might be present even in very notable quantity, and yet the peculiar color of its sulphide be entirely masked by the presence of organic matter.

Under these circumstances, the washed precipitate, placed in a thin porcelain dish, may be treated with a few drops of concentrated nitric acid, and the mixture cautiously evaporated to dryness, the operation being repeated, if necessary, until the organic matter is well destroyed. Any antimony present will now exist as an oxide of the metal. The residue is then moistened with a few drops of a strong solution of potassium hydrate, the liquid expelled by a moderate heat, and the dry residue very gradually heated to fusion. The cooled mass is stirred with a little water, the mixture acidulated with tartaric acid, then boiled for some minutes, and the solution filtered. The whole of the antimony will now be present in the filtrate, which, if the operations have been conducted with care, will be perfectly colorless. A portion or the whole of the solu-

tion may now be treated with a few drops of hydrochloric acid and exposed to a current of sulphuretted hydrogen gas, when any sulphide of antimony thrown down will exhibit its characteristic color.

By this method the sulphide of antimony produced from the 1–100th of a grain of the sesquioxide of the metal may be recovered from a very complex organic mixture without any apparent loss. Should the final solution obtained by the above method be highly colored, then, instead of treating it with sulphuretted hydrogen, it may be mixed with zinc and diluted sulphuric acid in the apparatus of Marsh, and the evolved gas conducted into a solution of silver nitrate, as long as a black precipitate is produced. Any antimonide of silver thus obtained is collected on a small filter and well washed; the point of the filter is then pierced, and the precipitate washed, by means of a jet of water from a wash-bottle, into a small dish, then boiled with a little tartaric acid, the solution filtered, and, after concentration if necessary, examined in the usual manner. The sulphide representing the 1–100th of a grain of sesquioxide of antimony may be carried through both these processes and still yield perfectly satisfactory results.

If it be desired, in case the investigation for antimony should fail, to provide for the detection of other poisonous metals whose sulphides are also precipitated from acidified solutions by sulphuretted hydrogen, such as arsenic, mercury, lead, and copper, the following method may be pursued. The filter containing the washed and still moist precipitate is spread out in a dish, the deposit well stirred with a solution of yellow sulphide of ammonium, and the solution filtered. As the sulphides of antimony and arsenic are readily soluble in sulphide of ammonium, these metals if present would be in the filtrate, while the sulphides of mercury, lead, and copper, being insoluble in this menstruum, would remain on the filter, which should therefore be reserved for future examination if necessary. The ammoniacal filtrate is now evaporated to dryness, and the residue treated with nitric acid and potassium hydrate in the manner already described. Any arsenic present would now exist as arsenate of potassium, and the solution when treated with sulphuretted hydrogen would yield a *yellow* precipitate of pentasulphide of arsenic. If this metal was not present, and the mixture contained antimony, the results already described would of course be obtained. Should these two metals

occur in the same solution, they may be separated by treating the mixture with zinc and sulphuric acid and receiving the evolved gas in a solution of silver nitrate, in the manner heretofore pointed out.

From the Tissues.—The investigations of Orfila and others have shown that antimony, when taken into the stomach, is rapidly absorbed by the blood and deposited in the tissues, and that the absorbed poison may be entirely eliminated from the living body within a very few days, the elimination taking place chiefly through the urine. Of the different tissues of the body, the liver and kidneys usually contain the largest proportion of the absorbed poison.

About one-third of the liver, cut into very small pieces and placed in a porcelain dish, may be made into a thin paste with water containing about one-fifth of its volume of pure hydrochloric acid. The mixture is then exposed to a moderate heat, with frequent stirring and the occasional addition of small quantities of powdered potassium chlorate, until the organic solids have become entirely disintegrated. The cooled mixture is transferred to a muslin strainer, and the organic matter left upon the cloth well washed with water, the washings being collected with the first-strained liquid; the solution is then filtered, the filtrate concentrated, allowed to cool, and if necessary again filtered. The solution is now exposed for several hours to a slow stream of sulphuretted hydrogen gas, after which it is allowed to repose for about twenty-four hours, in order that the precipitate may fully subside. Any precipitate thus obtained is collected, heated with nitric acid, then fused with potassium hydrate, and the residue examined in the manner described above.

For the recovery of absorbed antimony, Orfila recommended to decompose the organic matter by nitric and sulphuric acids. The tissue, cut into small pieces, is boiled with nitric acid, the homogeneous mixture evaporated to dryness, and the residue well charred with concentrated sulphuric acid. The dry carbonaceous mass is then boiled with hydrochloric acid containing a few drops of nitric acid, when any antimony present will be dissolved as chloride. The solution thus obtained is introduced into the apparatus of Marsh, and the evolved gas examined in the usual manner.

Absorbed antimony may also be recovered by boiling the finely divided tissue with pure hydrochloric acid diluted with about six volumes of water, and introducing into the boiling mixture separate

slips of bright copper-foil as long as they continue to receive a metallic coating. Only a small slip of the copper should at first be employed. Should this after several minutes fail to receive a deposit, it is removed from the mixture, and the boiling continued until the organic tissue is entirely disintegrated. The cooled mixture is then strained, and the strained liquid again boiled with a fresh slip of copper, the heat being continued if necessary until the liquid is evaporated to near dryness. It may be remarked that this method would not apply to organic mixtures which had been prepared by means of potassium chlorate, since the products of this salt would prevent the deposition of the antimony.

From the Urine.—Evaporate one thousand grains of the urine to a thick syrup; treat the residue on a water-bath with fuming nitric acid, portions at a time, until the urea is entirely destroyed, then evaporate to dryness. Moisten the residue with concentrated sulphuric acid, and heat on a sand-bath until the mass is dry and fumes of the acid no longer escape. Heat the powdered residue with about one hundred and twenty-five grains of water containing a few drops of hydrochloric acid until the soluble matter is exhausted; filter, and concentrate the filtrate to about eighty grain-measures. Treat the liquid with sulphuretted hydrogen, and gently warm the mixture: if the urine contained 1–250th grain or more of antimony, the precipitate produced will have a strongly marked red color.

Collect the precipitate on a small filter, and wash it with water, small portions at a time, until any calcium sulphate and other salts that may have separated are dissolved. Separate the portion of the filter containing the deposit from any unstained portion, and spread it in a porcelain dish; add a few drops of hydrochloric acid, and heat until the deposit has dissolved, then add a little water, squeeze and wash the paper. Filter, and treat the filtrate with sulphuretted hydrogen, when any antimony present, even if only in very minute quantity, will be precipitated as sulphide of its characteristic color.

By this method we have recovered the 1–1000th of a grain of antimony from one thousand grains of urine (1 : 1,000,000) without any very marked loss.

In a series of experiments on the elimination of this metal by means of the urine, conducted in the University laboratory by Dr. Wm. R. Hock (*Thesis*), single doses of ten milligrammes (about one-

sixth grain) each of antimony in solution were taken or administered. In one instance the urine voided within *five minutes* after the dose had been taken furnished satisfactory evidence of the presence of the metal; and in several instances it was detected in from ten to fifteen minutes after being taken. The greatest elimination seemed to take place within from one to two hours, after which it gradually diminished, but traces were still found as late as ninety-six hours after the dose had been taken.

Quantitative Analysis.—The pure solution, acidulated with hydrochloric acid, is treated with sulphuretted hydrogen gas as long as a precipitate is produced, and the mixture gently warmed until the supernatant liquid has become perfectly clear. The precipitate is then collected on a filter of known weight, washed, thoroughly dried on a water-bath, and weighed. Every one hundred parts by weight of sesquisulphide of antimony thus obtained correspond to 85.88 of the sesquioxide, or 196.47 parts of pure crystallized tartar emetic.

CHAPTER V.

ARSENIC.

I. Metallic Arsenic.

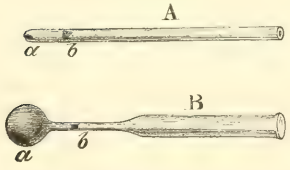
History and Chemical Nature.—By the term *arsenic* the chemist understands a certain simple or elementary form of matter, having metallic properties; this term, however, is popularly applied to an oxide of the metal,—arsenious oxide. The symbol for arsenic is As; and its atomic weight 75. Arsenic is found in nature in certain localities in its free state; in combination it is widely distributed, being found in certain minerals and ores, and in minute traces in many mineral waters and their ferruginous deposits. The statement formerly made by Orfila, that arsenic occurred as a normal constituent in the bones and muscles of animals, was afterward retracted as incorrect.

In its pure state arsenic has a steel-gray color, a bright metallic lustre, and a density of about 5.8; it has a crystalline structure, and is readily reduced to powder, being very brittle. It remains unchanged in dry air; but in the presence of moisture it slowly absorbs oxygen and assumes a dull dark-gray appearance. When heated, it volatilizes, without fusing, into a colorless vapor, which on coming in contact with the air emits a garlic-like odor; if strongly heated in the open air, it takes fire and burns with a bluish flame and the evolution of dense white fumes of arsenious oxide. It is generally stated that arsenic volatilizes at a temperature of about 182° C. (360° F.), but, according to Dr. Guy, when in small quantity, it sublimes at 110° C. (230° F.). Hot sulphuric and nitric acids oxidize and dissolve the metal, the former as arsenious and the latter as arsenic acid. Hydrochloric acid has no action upon it; but free chlorine converts it into chloride of arsenic.

Physiological Effects.—Metallic arsenic, when taken into the system, is capable of acting as a powerful poison; but perhaps only in so far as the metal becomes oxidized and converted into arsenious acid. From the experiments of Bayen and Deyeux, and others, it would appear that the metal in its uncombined state is inert. The substance sold in the shops under the name of fly-powder consists essentially of a mixture of metallic arsenic and arsenious oxide, the latter usually being present, it is said, in the proportion of about five per cent. Numerous instances of poisoning by this substance have occurred, chiefly, however, as the result of accident. In a case of criminal poisoning by fly-powder, in which we were consulted, death took place in thirty-six hours; and although there had been almost incessant vomiting for over thirty hours, a quantity of arsenic equivalent to forty-two grains of arsenious oxide remained in the stomach at the time of death. The symptoms and morbid changes produced by this substance are much the same as those occasioned by arsenious oxide.

Special Chemical Properties.—There is little difficulty in recognizing metallic arsenic. When volatilized in a narrow reduction-tube it condenses in the cooler portion of the tube, forming a very characteristic sublimate. This sublimate usually consists of two well-defined but conjoined parts, the lower of which has a steel-like appearance, and when viewed on the inside presents a crystalline structure, resembling somewhat that of fractured iron; the upper part of the deposit, when viewed exteriorly, is destitute of lustre, and of a dark color, which gradually fades into a light-gray margin, in which crystals of arsenious oxide are sometimes found. When the sublimate is quite thin it presents a brown appearance. On the application of heat, the sublimate is readily chased up and down the tube, and sooner or later becomes converted into white, octahedral crystals of arsenious oxide; this conversion is much hastened if the closed end of the tube has been separated. These reactions are peculiar to arsenic.

Fig. 4.



Tubes for sublimation of arsenic.

If metallic arsenic be dissolved, by the aid of heat, in strong nitric acid, and the solution evaporated to dryness, it leaves a white

residue of arsenic oxide, which, when moistened with a strong solution of silver nitrate, assumes a brick-red color. A portion of the arsenic oxide obtained by this method may be dissolved in water and submitted to the liquid tests for this acid, mentioned hereafter; or, the solution may be saturated with sulphurous oxide gas (SO_2), the excess of the gas expelled by heat, and the solution then examined for arsenious acid.

Compounds of Arsenic.—Arsenic forms with *oxygen* two well-defined oxides,—namely, arsenious oxide, As_2O_3, and arsenic oxide, As_2O_5. The *hydrates* of these oxides are known respectively as *arsenious acid* and *arsenic acid.* A lower, or suboxide, has been described, but its existence is doubtful. Arsenic unites with *sulphur* in several proportions; the most important of these compounds are disulphide of arsenic, or *Realgar*, As_2S_2, which has a ruby-red color; sesquisulphide of arsenic, or *Orpiment*, As_2S_3, having a bright yellow color; and pentasulphide of arsenic, As_2S_5, the color of which closely resembles that of orpiment. With *hydrogen* the metal forms arsenuretted hydrogen, or hydrogen arsenide, AsH_3, which is a colorless, highly poisonous, gaseous compound. With *chlorine* it forms trichloride of arsenic, $AsCl_3$. Arsenic also enters into various other combinations.

All the soluble compounds of this metal, and such insoluble combinations as undergo decomposition when taken into the system, are poisonous. As a general rule, their activity in this respect is in proportion to their solubility. Some of the insoluble compounds as usually met with not unfrequently contain arsenious oxide. This is the only compound of the metal that will be considered in detail; in its consideration, however, the chemical properties of several of the other compounds will be very fully described.

II. Arsenious Oxide.—Arsenious Acid.

Arsenious oxide, commonly called *white arsenic,* and also known as *ratsbane,* is a compound of two atoms of arsenic with three of oxygen, As_2O_3; its molecular weight is 99. It is readily obtained by volatilizing metallic arsenic in a free supply of air. For commercial purposes, it is usually prepared by roasting some one of the ores of the metal in a reverberatory furnace communicating with large chambers, in which the oxide condenses.

Arsenious oxide is found in the shops under two different forms,

—either as a white or dull white, opaque powder, or in the form of large, hard masses. If recently prepared, these masses are colorless and transparent; but on exposure to the air they become opaque and of a white or yellowish-white color. This change from the transparent to the opaque state has been ascribed to the absorption of moisture.

The *powder*, as found in the shops, when examined under the microscope, is sometimes wholly *amorphous*, consisting of very fine dust and small fragments, it being prepared simply by pulverizing the large masses. At other times it consists in part or wholly of minute *octahedral crystals*, these ranging in size from about 1–250th to 1–5000th of an inch in diameter. Hence the microscopic character of the powder—as to whether crystalline or not, the relative proportion of crystals to amorphous matter, and the prevailing size of the crystals or lumps—may in some instances enable us to determine with great certainty that a given sample was *not* derived from a certain source or supply. It has been found by several observers that great uniformity generally exists among samples of the powder taken from the same source, as from different and distant parts of the same keg. For examinations of this kind, it is best to mount a small portion of the powder in Canada balsam.*

Arsenious oxide, whether in the solid state or in solution, seems to be nearly or entirely destitute of *taste*. At least, it has frequently been swallowed in large quantity without any marked taste being perceived; in other instances, however, its taste has been variously described as sweetish, rough, hot, acrid, or metallic.

Symptoms.—These are subject to great variation. Sooner or later after a large dose of the poison has been swallowed there is usually a sense of heat and constriction in the throat, with thirst, nausea, and burning pain in the stomach. The pain becomes excruciating, and is attended with violent vomiting and retching; the matters vomited present various appearances, being sometimes streaked with blood, and at other times of a bilious character; the pain in the stomach is increased by pressure. As the case progresses, the pain extends throughout the abdomen, and there is generally severe

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* For a very full consideration of the microscopic differences observed in samples of commercial arsenic, we would refer the reader to a valuable paper by Prof. E. S. Dana, of New Haven. (*Pamphlet*, 1880.)

purging and tenesmus; the matters passed from the bowels not unfrequently contain blood. The thirst usually becomes very intense; in some instances there is great difficulty of swallowing. The features are collapsed and expressive of great anxiety; the pulse is quick, small, and irregular; the eyes red; the tongue dry and furred; the skin cold and clammy, but sometimes hot; the respiration difficult; and sometimes there are violent cramps of the legs and arms. The urine is frequently diminished in quantity, and its passage attended with great pain. Stupor, delirium, paralysis, and convulsions have also been observed. In many instances death takes place calmly, and the intellectual faculties remain clear to the last.

Such are the symptoms usually observed in poisoning by arsenic; but cases are reported in which the abdominal pain, thirst, vomiting, and purging were either very slight or entirely absent. In these instances the symptoms are usually not very unlike those commonly observed in poisoning by a narcotic. There is generally great prostration of strength, and faintness, or even actual syncope; often convulsions, and sometimes delirium or insensibility. It was formerly believed that well-marked gastric symptoms were absent only when a very large dose of the poison had been taken; but this is by no means always the case.

In a case of arsenical poisoning mentioned by Dr. Christison, an individual expired in five hours without at any time having vomited, although emetics were administered. The following case of this kind is reported by Mr. Fox. (*Lancet*, London, Nov. 4, 1848.) A stout, healthy young man took a teaspoonful of arsenious oxide, mistaking it for flour. No marked symptom of the action of the poison appeared for nearly six hours afterward, when purging suddenly supervened, and he vomited two or three times. He then became drowsy; countenance sunken and livid; pulse rapid and extremely feeble; surface of the body cold, and watery stools of a greenish hue passed involuntarily. He answered questions rationally, and did not complain either of pain, tenderness of the abdomen, tenesmus, or any of the usual irritative symptoms of arsenical poisoning. Soon afterward he complained of dimness of sight, lay down on the bed, and in a few minutes expired.

In most cases of acute poisoning by this substance the symptoms steadily run their course; yet sometimes there is a remission or even an entire intermission of the more prominent symptoms. This

remission may extend through a period of several hours, and the symptoms then return with increased violence. The remission has even been repeated several times in the same case.

The following singular case is related by Dr. C. U. Shepard, of South Carolina. (*Pamphlet*, 1878.) An intemperate man purposely swallowed, towards evening, about an ounce of arsenic. Immediately after taking the draught he vomited considerably, and during the night at intervals. The next morning he went into the street, having up to that time experienced little or no pain. About an hour later, however, he was seized with severe pains in the epigastrium, and fell on the pavement in great agony. After a few hours the pain subsided, and he was comparatively well. But several hours later he was again seized with violent pain in the stomach, and with excessive vomiting and purging. Wild delirium and general convulsions then supervened, and terminated fatally about twenty-four hours after the poison had been taken.

Considerable variety has also been observed in regard to the *time* within which the symptoms first manifest themselves. In most instances, however, they appear in from half an hour to an hour after the poison has been taken. In the case just related, there was, according to the statement of the patient, immediate vomiting. And in a case cited by Dr. Beck, a woman, who had swallowed a quantity of the poison mixed with wine and an egg, experienced extreme distress *immediately* after taking the mixture. (*Med. Jur.*, ii. 595.) In another instance, quoted by the same writer, twelve persons in one family were seized with symptoms immediately after eating some soup containing the poison. Dr. Christison quotes a case in which the symptoms appeared in eight minutes; and two others in which violent symptoms were present in ten minutes after the poison had been taken.

On the other hand, instances are related in which the symptoms were delayed much beyond the usual period. A case of this kind, in which they did not appear for nearly *six hours*, has already been cited. In a case related by Dr. Ryan, where half an ounce of arsenic was taken in porter, the first symptom, which was vomiting, did not occur until *nine hours* afterward. (Wharton and Stillé, *Med. Jur.*, 513.) A case is also quoted by Dr. Taylor, from Belloc, in which *ten hours* elapsed before any symptoms appeared. (*On Poisons*, 359.) And Dr. Wood mentions an instance (*U. S. Dispensatory*, 1865, 26),

related by Dr. E. Hartshorne, in which at least a drachm of arsenious oxide had been swallowed, and where the symptoms of poisoning were delayed for *sixteen hours*. This seems to be the most protracted case, in this respect, yet recorded.

The *external application* of arsenic to abraded surfaces has not unfrequently been followed by fatal results. In a case reported by Dr. McCready, a wash composed of a mixture of arsenious oxide and gin, applied to the head of a child two years old, affected with porrigo favosa, caused death in about thirty-six hours. The most prominent symptoms were swelling of the face, purging and tenesmus, and paralysis of the lower extremities. No local inflammation was produced. Two other children who were similarly treated suffered with redness and swelling of the face; but they speedily recovered. (*Am. Jour. Med. Sci.*, July, 1851, 259.) Dr. Christison cites an instance in which the stearine of a candle containing arsenic, applied to a blistered surface, produced local pain, nausea, pain in the stomach, great thirst, redness of the tongue, spasms of the muscles of the lower extremities, and weakness and irregularity of the pulse, followed by death within twenty-four hours after the application had been made.

In a series of cases recently reported (1878), a mixture sold as *violet powder*, containing nearly fifty per cent. of arsenic,—ignorantly substituted for *gypsum*, and this used instead of starch,—applied externally to some twenty-eight infants, caused death in thirteen instances. All the children suffered more or less from the application. The symptoms were a reddened condition of the skin, which soon became blue or black, and vesicated; there was great restlessness, with fits of screaming, followed by collapse and quiet death. The average duration of the fatal cases was from four to five days.

Arsenic has also proved fatal when applied to the mucous membrane of the *vagina* and of the *rectum*, and when inhaled in the form of *vapor*. In a case reported by Dr. Mangor, a man poisoned three wives in succession by introducing arsenic into the vagina. In at least two of these instances the poison produced its usual symptoms and death in twenty-four hours. Within late years numerous instances of *chronic poisoning* by this substance have occurred from persons occupying rooms hung with paper stained with *Scheele's green*, or arsenite of copper. From the examination of twenty-one cases of poisoning of this kind, Dr. Kirchgässer, of Coblentz, con-

cludes that the deleterious effects are due to the mechanical suspension of arsenical dust in the air of the apartment, rather than to the presence of a volatile arsenical compound, as some have supposed. (*Sydenham Soc. Year-Book*, 1869, 446.)

Period when Fatal.—In fatal poisoning by this substance, death usually occurs in from twelve to thirty-six hours after the poison has been taken. Numerous instances, however, are related in which death took place within a very few hours; while, on the other hand, life has not unfrequently been prolonged for several days. The most rapidly fatal case yet recorded is that communicated to Dr. Taylor, in which a youth, aged seventeen, died from the effects of a large dose of the poison within *twenty minutes* after it had been taken. (*Med. Jur.*, i. 256.) Dr. D. W. Finlay has recently reported a case fatal in *one hour* from the effects of a solution containing upwards of twenty-six grains of arsenious oxide. In this case there was profound collapse, with only slight symptoms of irritation. (*Lancet*, Dec. 1883, 943.) Not less than three instances fatal in *two hours* are reported. In a case related by Dr. Dymock, death occurred in two hours and a half; and Pyl relates another, which proved fatal in three hours. (*Christison on Poisons*, 240.) Ninety grains of the poison caused the death of a girl, aged fourteen years, in five hours. Several instances are reported in which the patients recovered from the primary action of the poison and died from its secondary effects very long periods afterward, even in one instance, related by Wepfer, after the lapse of three years.

Fatal Quantity.—According to the observations of Prof. Lachèse, of Angers, a dose of from one to two grains of arsenious oxide may prove fatal to a healthy adult; a dose of from a quarter to half a grain may induce symptoms of poisoning; and one-eighth of a grain may prove injurious. In a case quoted by Dr. Taylor, two grains of the poison, in the form of Fowler's solution, taken in divided doses during a period of five days, destroyed the life of a woman. The same writer cites another instance, reported by Dr. Letheby, in which two grains and a half killed a robust, healthy girl, aged nineteen, in thirty-six hours. (*On Poisons*, 377.) In a case mentioned by Dr. Christison, four grains and a half caused the death of a child, four years old, in six hours.

On the other hand, recovery has not unfrequently taken place after very large quantities of the poison had been swallowed. In a

case recorded by Dr. Pereira, a man swallowed half an ounce of powdered arsenic immediately after taking his dinner, and the only effect produced was violent vomiting. (*Mat. Med.*, i. 632.) So, also, Dr. A. Stillé (*Mat. Med.*, ii. 707) quotes the case of a woman who swallowed about a dessertspoonful of the poison immediately after a hearty meal, and although vomiting did not occur, nor were any remedies administered for an hour and a half, yet within five days complete recovery had taken place.

The following remarkable case is reported by Dr. W. C. Jackson. (*Am. Jour. Med. Sci.*, July, 1858, 77.) A young man, aged twenty-eight years, took on an empty stomach not less than *two ounces* of the poison. Nearly two hours afterward there was slight vomiting, with some traces of the arsenic; but the greater part of the poison was retained in the body for six hours. Great irritability of the stomach then ensued, with a burning sensation in this organ and in the throat. This condition continued for about six hours, after which the patient rapidly recovered.

In a case quoted by Prof. H. C. Wood (*Mat. Med. and Toxicol.*, 1874, 320), a man swallowed an unknown quantity of arsenic in lumps, and received no treatment for sixteen hours, yet recovered after passing per anum one hundred and five grains of arsenic in two masses.

Treatment.—This consists, in the first place, if there is not already free vomiting, in the speedy administration of an emetic, or the stomach may be emptied by means of the stomach-pump. As an emetic, sulphate of zinc or of copper may be employed; if neither of these is at hand, powdered mustard or a mixture of salt and water should be administered, or vomiting may be induced by tickling the throat with a feather. The vomiting should be assisted by the free exhibition of demulcent drinks. For this purpose a mixture of milk and white of egg has been found very beneficial. If the poison has passed into the bowels, a dose of castor oil may be highly useful.

Of the various chemical antidotes that have been proposed for arsenious acid, *hydrated ferric oxide*, known also as *hydrated sesquioxide of iron*, $Fe_2O_3,3H_2O$, is much the most important. Drs. Bunsen and Berthold, in 1834, were the first to assert the antidotal properties of this substance. When it is added to a solution of arsenious acid, the latter is rendered wholly, or very nearly, insoluble in water. In support of this statement we may adduce the

following experiments: 1. One grain of arsenious oxide, in solution, was agitated for a very little time with five grains of the iron preparation suspended in half an ounce of water, and the mixture quickly filtered. The filtrate was then examined and found to contain less than the 1–100th of a grain of the poison. 2. When ten parts of the iron preparation were employed, and the filtrate concentrated to one hundred fluid-grains, then acidulated with hydrochloric acid, and saturated with sulphuretted hydrogen gas, it failed to yield any distinct evidence of the presence of the poison, even after standing at a moderate temperature for several hours. These experiments do not, of course, prove that the compound thus produced is insoluble in the acid secretions of the stomach; yet the excess of the iron preparation administered might neutralize any free acid present.

The antidotal action of this substance is due to the *hydrated ferric oxide* yielding a portion of its oxygen to the arsenious acid, whereby the latter is converted into arsenic acid, which in turn unites with a portion of the iron, forming *arsenate of iron* ($Fe_3 2AsO_4$), which being insoluble is inert. Thus: $2Fe_2O_3,3H_2O + 2H_3AsO_3 = Fe_3 2AsO_4 + FeO + 9H_2O$. Theoretically, therefore, one part of arsenious oxide in solution as arsenious acid requires 2.16 parts of pure hydrated ferric oxide to render it inert. The antidote should, however, be given in its *moist* state, and be administered in large excess. It is usually stated that about twelve parts of the moist compound are required for one part of arsenious oxide. The antidote has no action upon arsenious oxide in its solid state, but only when in solution.

Hydrated ferric oxide may readily be prepared by treating *tincture of ferric chloride* of the shops, or a strong solution of ferric sulphate, with slight excess of ammonia, collecting the precipitate on a muslin strainer, and washing it with water until it no longer emits the odor of ammonia. A tablespoonful or more of the moist magma, mixed with a little water, may be given at a dose. The antidote should always be freshly prepared.

In this connection, we may very briefly refer to some experiments, kindly undertaken by Dr. Wm. Watt, with this antidote upon poisoned dogs. (For details, see *Ohio Med. and Surg. Jour.*, March, 1861.) The action of the poison alone was first determined upon five dogs of average size. To three of these, six grains of arsenious

oxide, in solution, were given to each, and proved fatal in one hour and a half, five hours, and six hours respectively. To the other two, three grains each were administered, and caused death in six and eight hours respectively. A solution of the poison was then administered to twelve other dogs, and the dose followed—in some instances immediately, in others in ten minutes, and in others still not until symptoms of poisoning had manifested themselves—by a single dose of about two tablespoonfuls of the antidote, prepared in the manner just described. After vomiting, in some instances only once, but in others several times, all these animals recovered, at most within several hours, and without in any instance suffering severe symptoms. Two of these dogs received three grains; two, four grains; one, five grains; three, six grains; two, seven grains; and two, eight grains each of the poison. In another experiment, six grains of the poison, in solution, were mixed with about fifteen parts by weight of the antidote, and the mixture, after standing twenty minutes, given to a dog; no appreciable effect whatever was observed, although the animal was closely watched for many hours. This experiment, therefore, indicates that the arsenate of iron is not readily decomposed by the juices of the stomach.

Numerous instances are reported in which there seems to be no doubt that this antidote was the means of saving life in the human subject. Mr. Robson relates an instance of this kind, in which more than a drachm and a half of the poison had been swallowed, and the antidote was not administered until two hours after the poison had been taken. In this case, about an hour after the ingestion of the poison, the stomach-pump was used, but unsuccessfully, on account of the instrument becoming choked with the remains of food. (*U. S. Dispensatory*, 1865, 29.) It need hardly be remarked that the antidote can have no effect upon any of the poison that has already entered the circulation.

Instead of the above antidote, R. V. Mattison has advised (*Am. Jour. Pharm.*, Jan. 1878, 23) a solution of *dialyzed iron*, followed immediately by the administration of common salt. According to E. Hirschsohn, of Dorpat, however, dialyzed iron is much less certain in its action than the *antidotum arsenici*, which consists of a mixture of hydrated ferric oxide, magnesium sulphate, and magnesium hydrate, being prepared by treating a solution of ferric sulphate with excess of magnesia.

In four cases of arsenical poisoning reported by Dr. C. A. Leale, of New York (*Am. Jour. Med. Sci.*, Jan. 1880, 80), he employed as an antidote the common *subcarbonate of iron* with good results, although in one instance fully one ounce of arsenious oxide, and in the others one-half ounce, one ounce, and two ounces respectively of Paris green had been taken.

Post-mortem Appearances.—Great variety has been observed in the appearances after death from arsenic, even in cases in which the symptoms during life were very similar. The lining membrane of the throat and œsophagus has in some few instances been found highly inflamed. The mucous membrane of the stomach is generally more or less reddened and inflamed; sometimes it has a deep crimson color, at other times it is of a deep brownish-red, and it has presented a dark appearance, due to the effusion of altered blood. This membrane is sometimes much softened, and easily separated; and in some instances patches of it are entirely destroyed. In other instances, however, it is much thickened and corrugated. The inflammation rarely extends to the peritoneal covering of the stomach. When the poison has been taken in the solid state, small particles of it are frequently found adhering to the mucous membrane and covered with coagulated mucus. Ulceration of the stomach has been of rare occurrence, except in protracted cases; however, Dr. Taylor observed it in a case that proved fatal in ten hours.

In protracted cases, the intestines, particularly the duodenum and rectum, not unfrequently present signs of inflammatory action similar to those found in the stomach. The lungs are sometimes congested and inflamed; congestion of the brain has also been observed. The blood throughout the body is usually liquid, and of a dark color.

Not a few instances of poisoning by this substance are recorded in which after death no well-marked morbid appearances were discovered in any part of the body. This result has even been observed in cases in which there were violent symptoms and life was prolonged for many hours.

In a case reported by Dr. A. R. Davidson (*Buffalo Med. and Surg. Jour.*, Oct. 1882, 117), in which an unknown quantity of the poison proved fatal in twelve hours, under the usual symptoms, to a boy aged six years, the mucous membrane of the stomach was slightly paler than normal, and wholly free from any appearance of inflammatory action; nor was any morbid change observed in any part of

the body. Something over half a grain of arsenious oxide was recovered from the liver and kidneys.

When the inspection is made some time after decomposition has been established, the stomach and intestines may present patches of a more or less bright yellow color, due to the conversion of the arsenic into sulphide by the sulphuretted hydrogen evolved in the putrefaction. This appearance may manifest itself within a few days after death, as we have observed in poisoned animals; whilst, on the other hand, even when very notable quantities of the poison are present, it may be absent after even very long periods. Indeed, it has recently been shown by J. Assikovszky (*Jour. prakt. Chem.*, 1880, 323) that during the process of putrefaction of organic bodies pure arsenious sulphide may be converted into arsenious and arsenic oxides.

Antiseptic Properties of Arsenic.—The preservative power of arsenic when brought in direct contact with animal textures is well known; and the poison seems to exert a similar action when carried by means of the circulation to the different tissues of the body. The bodies therefore of those who have died from the effects of this poison are not unfrequently found in a good state of preservation, even long periods after death.

We have elsewhere reported a case, described by Dr. Douglas Day, in which this preservative action of the poison was well marked in a body that had been buried *seventeen months.* At this time the body was destitute of odor, and the flesh of the extremities had given place to a dark unctuous matter. The abdominal walls were in a surprising state of preservation, and of the color of old parchment; the integuments upon incision were firm, and the muscles of a pink hue, but very attenuated. The omentum was large and in place, and covered with saponaceous matter. The stomach and intestines were pale, comparatively dry, and appeared as though the convolutions had been pressed together; they were firm and allowed free manipulation, and exhaled a peculiar but not offensive odor. The liver, spleen, and pancreas appeared remarkably recent, and the posterior walls of the abdomen, the mesentery, and kidneys were well preserved. The bladder also was in a good state of preservation. A very notable quantity of arsenic was detected in each of several of the abdominal organs: no other parts were submitted to chemical examination. (*Ohio Med. and Surg. Jour.*, Nov. 1863.)

In another case in which we made the chemical examination in 1871, that of Peter Buffenbarger, of Ohio, the body when exhumed, at the end of *three years and a half*, "was found entire and in a remarkable state of preservation." "The tissues were quite firm and solid; the liver entire, but easily broken up; the stomach was fresh and parchment-like; the walls of the abdomen firm." Very satisfactory evidence of the presence of arsenic in minute quantity was obtained both from the stomach and the liver. These were the only organs furnished for chemical analysis. At a preliminary hearing of this case, it was urged by the defence that the poison had been injected into the body after death. It was clearly shown, however, that the vault in which the body was buried had not been disturbed from the time it was first closed; and there was no evidence whatever that the poison had been injected before burial.

Dr. Christison quotes a case in which the body after being interred *seven years* was found entire. The head, trunk, and limbs retained their situation; but the organs of the chest and abdomen were converted into a brown soft mass, in which a chemical analysis revealed the presence of a considerable quantity of arsenic.

Although the bodies of those who died from the effects of this poison have thus been found in an unusual state of preservation, yet this is by no means always the case, even when the poison remains in the body at the time of death. In fact, in some cases of arsenical poisoning the process of putrefaction seemed to advance with increased activity. At the same time, it must be borne in mind that the body is sometimes unusually preserved in cases in which death resulted from ordinary disease or mechanical injury.

Chemical Properties.

General Chemical Nature.—It has already been stated that arsenious oxide, in its amorphous state, occurs under two varieties, known as the transparent and the opaque. The specific gravity of the transparent variety seems to be some little greater than that of the opaque, the density of the former, according to most observers, being about 3.75, and that of the latter about 3.65. These varieties also differ in regard to their solubility in water. According to most observers, arsenious oxide volatilizes at about 191° C. (380° F.); but, according to Dr. Guy, it may be vaporized, especially if in minute quantity, at 138° C. (280° F.). The vapor is colorless and odorless,

and recondenses unchanged on cold surfaces, principally in the form of regular octahedral crystals. (For an excellent paper on the crystalline forms of arsenious oxide, by Dr. Guy, see *Quart. Jour. Micro. Science*, July, 1861.)

Arsenious oxide is soluble in water with the formation of *arsenious acid*, each molecule of the former assimilating the elements of three molecules of water to form two molecules of the acid; thus: $As_2O_3 + 3H_2O = 2H_3AsO_3$. This acid, which is tribasic, has, however, not yet been obtained in the free state.

Arsenious acid has only feebly acid properties; nevertheless it readily unites with many of the metals, forming salts denominated *arsenites*. These salts are readily decomposed by most other acids. The arsenites of the alkali metals are freely soluble in water; but all other arsenites are either insoluble or only sparingly soluble in this menstruum. The latter salts are readily decomposed and dissolved by nitric and hydrochloric acids. Upon the application of heat, most of the arsenites undergo decomposition. In this operation the fixed alkali arsenites retain the greater portion of the arsenic, in the form of an *arsenate*. When ignited with a reducing agent, all arsenites are decomposed, with the evolution of metallic arsenic in the form of vapor.

Solubility. 1. *In Water.*—The degree of solubility of *arsenious oxide* in water sometimes becomes a matter of considerable importance in medico-legal investigations. The results of observers in regard to this point have been extremely discordant. The exact quantity of the poison that will be taken up and retained in solution by a given quantity of water will depend upon a variety of circumstances, among the principal of which are the following: 1. The physical state of the oxide; 2. The relative proportions of the oxide and water present; 3. The time they have been in contact; 4. The temperature of the mixture; 5. If the mixture has been boiled, the length of time the boiling was continued; and, 6. The time that has elapsed since the mixture was heated. Among numerous experiments that might be cited showing the influence of these various conditions, the following may be mentioned:

a. One part (50 grains) of finely powdered *opaque* arsenious oxide was boiled with ten parts (500 grains) of distilled water for one hour, the vaporized fluid being condensed and returned to the flask as rapidly as formed, and thus the volume of the fluid kept con-

stantly the same. The solution was then filtered as rapidly as possible, and a given portion of the filtrate evaporated to dryness on a water-bath. The residue thus obtained indicated that one part of the oxide had dissolved in 13.10 parts of water.

b. A similar experiment with the *transparent* variety of the oxide, taken from the same mass as employed in experiment *a*, gave a residue indicating that one part of the oxide had dissolved in 15.66 parts of water. According to Bussy, the transparent variety is more soluble than the opaque; Guibourt, however, states that the reverse is the fact.

c. A similar experiment with the freshly sublimed *crystallized* oxide indicated that one part of the oxide had dissolved in 11.50 parts of water.

d. On repeating the last experiment and concentrating the filtering solution to about half its volume, a white scum appeared upon the surface of the liquid. The clear liquid was then decanted and a given portion evaporated to dryness, when it was found that one part of the oxide had been held in solution by 6.72 parts of water.

e. After boiling one part of the crystallized oxide, from the sample used in experiment *c*, for one hour with ten parts of pure water, without loss of liquid by evaporation, the mixture was allowed to stand twenty-four hours. The solution then contained one part of the oxide in 58.68 parts of water.

f. One part of the *opaque* oxide, from the sample used in experiment *a*, was boiled for one hour with *forty* parts of water, without loss of liquid by evaporation, and the solution quickly filtered. The filtrate contained one part of the oxide in 43.7 parts of the menstruum. It will be observed that in this experiment the conditions were the same as in experiment *a*, except in the relative proportion of oxide and water present. Even when one part of the oxide is boiled for an hour with one hundred parts of water, a portion of the poison will still remain undissolved.

g. One part of the opaque oxide was treated with twenty parts of boiling water and the mixture frequently agitated for twenty-four hours. The solution then contained one part of the oxide in 196 parts of water.

h. On treating the *transparent* variety of the oxide in the same manner as in the last experiment, the solution contained one part of the poison in 93 parts of the menstruum. On comparing the experi-

ments *g* and *h* with those of *a* and *b*, it will be observed that under one set of conditions the transparent oxide dissolved more freely than the opaque variety, whilst under another the reverse was the case.

i. One part of the *crystallized* oxide was frequently agitated during nine days, at the ordinary temperature, with *twenty* parts of pure water. The resulting solution contained one part of the oxide in 108 parts of water.

j. An experiment similar to the last and conducted at the same time, with one part of the oxide and *five hundred* parts of water, yielded a solution which contained one part of oxide in 810 parts of the menstruum.

The experiments now cited serve to explain, at least in a measure, the discrepant statements of observers in regard to the solubility of this substance. Furthermore, it is obvious that unless something is known in regard to the conditions under which the oxide and liquid have been brought in contact, it will be impossible to state even approximately how much of the poison may have been dissolved, even by pure water. In general terms, if the mixture contained one part of the oxide to ten or twelve parts of water and has been boiled and concentrated, the liquid may hold in solution even as much as one-seventh of its weight of the poison; whilst, on the other hand, if there was very large excess of water and the mixture was not heated, the liquid may not take up more than the 1–1000th of its weight of the oxide.

Gmelin placed pulverized opaque arsenious oxide in various proportions of water in closed bottles, and set them aside in a cool place for eighteen years, with the following results. One part of the oxide in 1000 parts of water: perfect solution. One part of the oxide in 100 parts of water: the solution contained one part of oxide in 102 parts of water. One part of oxide in 35 parts of water: the solution contained one part of the oxide in 54 parts of water. (*Hand-book of Chemistry,* iv. 257.)

According to most observers, the solubility of the poison is more or less diminished by the presence of most kinds of organic matter.

In an ordinary decoction of coffee, to which during its preparation white arsenic had been criminally added, Dr. C. McIntire found one part of the oxide in solution in thirty-nine parts of the menstruum; and by experiment he found that one part of the oxide

might be taken up by about twenty parts of the decoction. (*Proc. Am. Chem. Soc.*, 1878, 56.)

2. *In Alcohol.*—One part of the crystallized oxide, in the state of powder, was frequently agitated for two days with twenty parts of alcohol of specific gravity 0.802 (= 97.5 per cent.). The solution thus obtained contained one part of oxide in 2000 parts of the menstruum. In a similar experiment with the most common kind of *whiskey*, one part of the oxide dissolved in 880 parts of the liquid.

3. *In Chloroform.*—On frequently agitating powdered arsenious oxide for two days with twenty parts by weight of pure chloroform, two hundred grains of the filtered liquid contained something less than the 1–1000th of a grain of the oxide. This experiment would, therefore, indicate that the oxide required more than 200,000 times its weight of chloroform for solution.

Absolute ether, under the conditions just mentioned, failed to dissolve a trace of the poison.

Arsenious oxide is readily soluble in solutions of the fixed caustic alkalies, but it is much less soluble in ammonia. It is also soluble in hydrochloric acid, and in certain of the vegetable acids; sulphuric acid dissolves it only in minute quantity. Hot nitric acid oxidizes and dissolves it to arsenic acid.

Of Solid Arsenious Oxide.

1. If a small quantity of solid arsenious oxide be thrown on a piece of ignited charcoal or heated on a charcoal support in the reducing blow-pipe flame, it is dissipated in the form of white fumes and emits a garlic-like odor. In this operation the arsenious oxide first gives up its oxygen to the carbon, forming carbon dioxide gas; the metallic arsenic thus set free is then reoxidized by the air into arsenious oxide, which is evolved and gives rise to white fumes. The alliaceous odor emitted is due to the reoxidation of the metal, and is evolved only when the metal itself is being oxidized. It was formerly supposed that this odor was peculiar to arsenic, but it is now known that there are several other substances which evolve a similar odor.

2. When heated in a reduction-tube, arsenious oxide volatilizes without fusing and recondenses in the cooler portion of the tube, in the form of minute, octahedral crystals. Under the microscope, this sublimate is quite peculiar, and the crystals present the appearances

illustrated in Plate IV., fig. 5. When only a very minute quantity of the poison is thus sublimed, the crystals are exceedingly small, but still perfectly characteristic. Under an amplification of one hundred diameters, the angular nature of a crystal that does not exceed the 1–8000th of an inch in diameter may be readily recognized; and with a power of two hundred and fifty, crystals measuring only the 1–15,000th of an inch in size may be satisfactorily determined. If sufficient sublimate be obtained, the portion of the tube containing it may be boiled in a small quantity of pure water, and the solution thus obtained, after concentration if necessary, examined by the liquid tests mentioned hereafter.

In applying this test to only a minute quantity of arsenious oxide, the bore of the reduction-tube should not exceed the 1–16th of an inch in diameter. Or, after placing the oxide in a tube of this kind having thin walls, the tube may be carefully heated at a little distance above the point occupied by the oxide, in a small blow-pipe flame, and drawn out into a capillary neck; the oxide is then sublimed into the contracted portion of the tube. By this method the least visible quantity of the poison will yield a very satisfactory sublimate; at the same time, this method permits the application of the higher powers of the microscope for the examination of the sublimate.

Prof. Guy recommends (*Chem. News*, i. 200) to heat the arsenious oxide in a perfectly dry tube of small diameter and about three-quarters of an inch in length and having its mouth covered with a warm slide or disk of glass. The crystals are deposited partly on the sides of the tube, but chiefly on the glass cover. This method offers the advantage of having the deposit upon a flat surface for examination by the microscope; in point of delicacy, however, it is very far inferior to the preceding method.

In applying this sublimation-test to a suspected substance, it must be borne in mind that there are other white powders besides arsenious oxide, as salts of ammonium, oxalic acid, and corrosive sublimate, which when heated in a reduction-tube may yield a crystalline sublimate. But most, if not all, of these fallacious substances melt before volatilizing, and none of them condense in the form of octahedral crystals.

3. *Reduction Test.*

a. If a small quantity of arsenious oxide be placed in the closed end of a narrow reduction-tube, or in the end of a tube drawn out in

the form shown in Fig. 5, and a wedge of recently ignited charcoal, *b*, be placed in the tube a little distance above the arsenical fragment or powder, on heating the charcoal to redness by the flame of a spirit-lamp and then slowly erecting the outer end of the tube so that the flame may still heat the charcoal and at the same time volatilize the arsenious oxide, the latter will be *deoxidized* in its passage over the ignited charcoal and yield a sublimate, *c*, of metallic arsenic. This reduction may also be effected by mixing the arsenious oxide with a perfectly dry mixture of powdered charcoal and sodium carbonate, and heating the whole in a plain or bulbed reduction-tube.

Fig. 5.

Tube for the reduction of arsenious oxide by charcoal. One-third natural size.

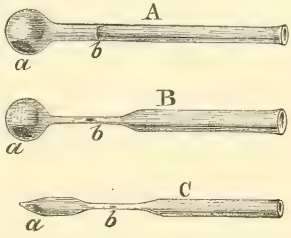
The sublimate thus obtained usually consists of two well-defined parts, the lower of which has a bright mirror appearance resembling polished steel; while the upper has a darker color, is destitute of lustre, and is gradually lost in a light-gray mist. The inner surface of the sublimate, especially of the lower ring, presents a bright crystalline appearance. Sometimes the upper portion of the sublimate, when very thin, has a brownish color. So, also, sometimes its upper margin contains crystals of arsenious oxide.

If the closed end of the tube be removed and the sublimate then heated, it is readily volatilized and oxidized into arsenious oxide, which condenses in octahedral crystals. The *metallic sublimate* is soluble in a solution of either sodium or calcium hypochlorite. This confirmatory test may be applied by removing the lower end of the tube, and then immersing the latter in a small quantity of the sodium solution; or, a few drops of the solution may be drawn into the tube, after the removal of its closed end, by suction with the mouth. The upper portion of the sublimate readily disappears when moistened with this liquid, but the lower part requires some little time for solution; sometimes the deposit becomes detached and drops out of the tube in the form of a metallic ring. The arsenical nature of the sublimate may also be shown by dissolving it in a few drops of warm nitric acid, evaporating the solution to dryness by a moderate heat, and touching the residue with a drop or two of a strong solution of silver nitrate, when it will assume a brick-red color, due to the formation of silver arsenate.

b. One of the best methods yet proposed for the reduction of

solid arsenious oxide, and one which is equally applicable for arsenites and the sulphides of arsenic, is by means of a *perfectly dry* mixture of about equal parts of *sodium carbonate* and *potassium cyanide*. A small portion of the arsenical compound is introduced into the bulb of a tube of the form shown in Fig. 6, A, or of the form B as first proposed by Berzelius, and covered with several times its volume of the above mixture. A gentle heat is then applied, first to the neck of the tube and afterward to the bulb; if in this operation any moisture condenses within the tube, it should be carefully removed. On now strongly heating the mixture, the compound under examination will be reduced and yield a metallic sublimate at about the point *b*. This reaction is extremely delicate, especially when performed in a Berzelius-tube.

Fig. 6.



Tubes for the reduction of arsenious oxide.

When only a very minute quantity of the arsenical compound is to be reduced, it may be placed in the closed end of an ordinary reduction-tube, covered by the reducing mixture, and the tube then heated at a little distance above the mixture in a blow-pipe flame, and drawn out into a contracted neck, as represented in Fig. 6, C. After the neck of the tube has cooled, the arsenical mixture is heated in the manner above described. A mixture containing only the 1–1000th of a grain of arsenious oxide, when treated after this method in a tube having its neck contracted to about the 1–20th of an inch in diameter, will yield a very satisfactory metallic sublimate, which upon resublimation farther up the neck of the tube will furnish several hundred crystals of arsenious oxide, many of them measuring the 1–1000th of an inch in diameter. Compounds of *antimony* yield no sublimate whatever when heated with the reducing mixture.

c. As a reducing agent for arsenious oxide, arsenites, and the sulphides of arsenic, as well as for other metallic compounds, Dr. E. Davy, of Dublin, has recommended potassium ferrocyanide, or yellow prussiate of potash, previously dried at a temperature of 100° C. (212° F.). (*Chemical News*, iii. 288.) This salt has an advantage over potassium cyanide, in that it does not readily absorb moisture from the atmosphere. The arsenical compound is mixed

with about six or eight times its volume of the dried salt, and the mixture fused in one or other of the reduction-tubes already described. The mixture blackens before fusing. In point of delicacy the reaction of this reducing agent is quite equal to that of potassium cyanide.

Fallacies.—When, by either of the above methods of reduction, a metallic sublimate having the physical and chemical properties described is obtained, there is no doubt whatever of the presence of arsenic. Compounds of *mercury*, *cadmium*, *tellurium*, and *selenium* may under similar circumstances yield sublimates. These, however, may be readily distinguished from the arsenical sublimate, even by the naked eye; under the microscope they would be found to consist of globules or drops. Moreover, neither of these sublimates when revolatilized will, like arsenic, furnish octahedral crystals; nor are they soluble in a solution of sodium hypochlorite. Neither will they, when dissolved in hot nitric acid and the solution evaporated to dryness, leave a residue which assumes a brick-red color when moistened with a solution of silver nitrate.

It has also been stated that a crust of charcoal or the employment of a reduction-tube containing lead might lead to error; but it is difficult to conceive how either of these results could be mistaken for an arsenical sublimate by any one at all conversant with the physical appearances of the latter.

Solutions of Arsenious Oxide.—Arsenious Acid.

Pure aqueous solutions of arsenious oxide have only a feeble acid reaction. This reaction is common to both varieties of the oxide, and is still manifest in a solution containing only the 1–1000th of its weight of the poison. On allowing a drop of a solution of this kind to evaporate spontaneously to dryness, for convenience on a glass slide, the oxide will be left chiefly in the form of white, octahedral crystals, which are readily dissipated by heat. The residue thus obtained from the 1–100th of a grain of the acid will usually contain many crystals that measure the 1–1000th of an inch in diameter. Equally satisfactory results may be obtained from the 1–1000th of a grain of the oxide, but the crystals are usually quite small. From the 1–10,000th of a grain of the oxide the crystals are very minute, but under the higher powers of the microscope their true nature may be very satisfactorily determined. The production

of these octahedral crystals, completely vaporizable by heat, is peculiar to arsenious oxide. The dry residue thus obtained may, of course, be examined by any of the tests already mentioned for the poison in its solid state.

In the following investigations in regard to the behavior of solutions of arsenious oxide, solutions of the pure crystallized oxide were employed. The fractions indicate the amount of anhydrous oxide present in *one grain* of the solution. The results, unless otherwise stated, refer to the reactions of one grain of the solution.

1. *Ammonio Silver Nitrate.*

This reagent is prepared by cautiously adding a dilute solution of ammonia to a solution of silver nitrate, until the merest trace of the precipitate first produced remains undissolved. It is important that the proper quantity of ammonia be added: since if there is deficiency, the reagent will also produce yellow precipitates with solutions of the alkali phosphates and silicates; whilst, on the other hand, if there is excess, it occasions no precipitate, or only a partial one, with arsenious acid. The reagent should always be freshly prepared. Nitrate of silver alone produces at most only a slight turbidity in solutions of free arsenious acid; but with neutral arsenites it behaves in the same manner as the ammonio-nitrate with the free acid. This test was first proposed, in 1789, by Mr. Hume, of London.

Ammonio silver nitrate throws down from aqueous solutions of arsenious acid a bright yellow precipitate of tribasic silver arsenite, Ag_3AsO_3, the reaction being, perhaps, $2H_3AsO_3 + 6AgNH_3NO_3 = 2Ag_3AsO_3 + 6NH_4NO_3$. According to some observers, however, the reagent has the composition $AgNH_2,NH_4NO_3$, and the reaction is $2H_3AsO_3 + 6AgNH_2,NH_4NO_3 = 2Ag_3AsO_3 + 6NH_4NO_3 + 6NH_3$.

The precipitate is readily soluble, to a colorless solution, in ammonia and in nitric and acetic acids, sparingly soluble in ammonium nitrate, and insoluble in the fixed caustic alkalies. After a little time the precipitate becomes more or less crystalline, and is then *insoluble* in ammonia and in acetic acid. Hydrochloric acid decomposes the precipitate with the formation of white insoluble silver chloride.

1. $\frac{1}{100}$ grain of arsenious oxide, in one grain of water, yields with the reagent a copious, bright yellow, amorphous precipitate, which after a little time becomes converted into yellowish-brown crystals, of the forms illustrated in Plate IV., fig. 6. The crystals

closely adhere to the glass upon which they have formed, and are insoluble in large excess of ammonia and of acetic acid.

2. $\frac{1}{1000}$ grain yields a rather copious precipitate, which partly becomes crystalline.
3. $\frac{1}{5000}$ grain: a quite good deposit, which remains amorphous.
4. $\frac{1}{10,000}$ grain: an immediate yellowish turbidity, and in a little time small yellow flakes.
5. $\frac{1}{25,000}$ grain: after a little time the mixture becomes very distinctly turbid, and when viewed over a white surface, as white paper, presents a slight yellow tint. Ten grains of the solution yield an immediate yellowish turbidity, and after a little time small flakes having a decided yellow color. When examined in large quantity, solutions even much more dilute than this will yield very distinct reactions.

If the silver arsenite thrown down by this reagent be decomposed by slight excess of hydrochloric acid and the silver chloride separated by a filter, the clear acid filtrate will yield with sulphuretted hydrogen gas a bright yellow precipitate of arsenious sulphide, having the properties to be pointed out hereafter. When the silver arsenite is washed, thoroughly dried, and heated in a reduction-tube, it undergoes decomposition with the production of a sublimate of octahedral crystals of arsenious oxide; when heated in a similar manner with a reducing agent, such as potassium ferrocyanide, it yields a sublimate of metallic arsenic. By either of these methods the arsenical nature of very minute quantities of the silver precipitate may be fully established.

Fallacies.—Ammonio silver nitrate also produces in solutions of *free phosphoric acid* a yellow, amorphous precipitate, which is readily soluble in nitric acid and in ammonia; this precipitate always remains amorphous. So, also, the reagent produces a somewhat similar precipitate in solutions of free *vanadic acid;* but these solutions, unlike those of arsenious acid, have a yellow color. Both free phosphoric and vanadic acids, especially the latter, are extremely rare, and therefore not likely to be met with in medico-legal investigations. The properly prepared reagent fails to produce a precipitate in solutions of the *salts* of either of these acids. Again, solutions of the alkali iodides and bromides yield with the reagent yellowish precipitates; but these precipitates are *insoluble* in dilute nitric acid, and only slightly soluble in caustic ammonia.

It need hardly be remarked that neither of the above precipitates, when dried and heated either alone or with a reducing agent, in a reduction-tube, will yield an octahedral or metallic sublimate. Neither of the above acids is a source of fallacy to any of the other tests for arsenic.

Should arsenious acid and a chloride, as common salt, occur in the same solution, the latter compound will yield with the silver reagent a white precipitate of silver chloride, which will obscure the arsenical reaction. From a mixture of this kind the chlorine may be removed by treating the solution, after the addition of a drop of nitric acid, with slight excess of pure silver nitrate, and filtering. On now exactly neutralizing the filtrate with ammonia, the yellow silver arsenite will separate.

Since ammonio silver nitrate is decomposed with the production of a precipitate, even in the absence of arsenious acid, by most organic solutions, the test is not applicable to mixtures of this kind.

2. *Ammonio Copper Sulphate.*

This reagent is prepared by cautiously adding ammonia to a somewhat dilute solution of copper sulphate, until the precipitate first produced is very nearly all redissolved; the clear liquid is then decanted. The reagent produces in solutions of arsenious oxide a green, amorphous precipitate of copper arsenite ($CuHAsO_3$), known also as *Scheele's green*, the reaction being, perhaps, $2H_3AsO_3 + 2CuH_2O_2(NH_3)_2,(NH_4)_2SO_4 = 2CuHAsO_3 + 2(NH_4)_2SO_4 + 4NH_4HO$. Chemists, however, are by no means fully agreed as to the exact composition of Scheele's green.

The precipitate is nearly insoluble even in large excess of the precipitant, but readily soluble in ammonia and in free acids. From very dilute solutions of the poison the precipitate does not appear of its characteristic color until the mixture has stood for some time. The same precipitate is thrown down from solutions of neutral arsenites by copper sulphate alone.

1. $\frac{1}{100}$ grain of arsenious oxide, in one grain of water, yields a very copious, yellowish-green precipitate, which when washed acquires a bright green color.
2. $\frac{1}{1000}$ grain: a rather copious, green deposit.
3. $\frac{1}{5000}$ grain: a good, bluish-green precipitate, which after a little time assumes a distinct green color, the blue tint disappearing.

The true color of these precipitates is best seen when examined over a white surface.

4. $\frac{1}{10,000}$ grain: an immediate bluish flocculent precipitate, which after a little time acquires a light green color. The precipitate from ten grains of the solution soon acquires a fine green color.

Ten grains of a 1–25,000th solution of the oxide yield an immediate blue precipitate, which in a little time acquires a light green hue.

Fallacies.—There is no other metallic substance, besides arsenic, known that yields with this reagent a similar precipitate. But various organic substances yield with the reagent a precipitate having in some instances a color somewhat resembling that of the arsenite of copper. So far, therefore, as the mere production of a greenish precipitate is concerned, no reliance whatever could be placed in the tests when applied to organic solutions.

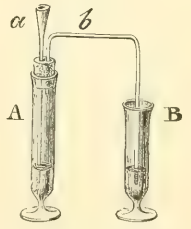
The arsenical nature of copper arsenite may be shown by heating the dried precipitate, either *alone* or with a *reducing agent*, in a reduction-tube, when it will yield a sublimate of octahedral crystals of arsenious oxide or of metallic arsenic, as the case may be. When dissolved in hydrochloric acid and boiled with a slip of bright copper-foil, arsenite of copper is decomposed, with the deposition of metallic arsenic upon the copper-foil: the true nature of this deposit may be shown in the manner to be described hereafter, under the consideration of Reinsch's test. If the hydrochloric acid solution of the arsenite be treated with sulphuretted hydrogen gas, it will yield a brown or dark-brown precipitate, consisting of a mixture of the sulphides of arsenic and copper. If this precipitate be collected on a filter, washed, and then digested with ammonia, the latter will dissolve the arsenious sulphide, while the copper sulphide will remain undissolved. On now filtering the ammoniacal solution and carefully neutralizing it with hydrochloric acid, the arsenious sulphide will separate in the form of a bright yellow precipitate.

3. *Sulphuretted Hydrogen.*

Sulphuretted hydrogen gas, or *Hydrosulphuric acid*, throws down from solutions of arsenious acid, previously acidulated with hydrochloric acid, a bright yellow, amorphous precipitate of arsenious sulphide, or sesquisulphide of arsenic, As_2S_3, known also as *Orpiment*, the reaction being $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$. For the

application of this test, a small quantity of iron sulphide may be introduced into an ordinary gas-evolution flask and covered with pure water; the mouth of the flask is then closed by a cork having two perforations, one of which carries a funnel-tube, and the other an exit-tube bent twice at right angles. Sufficient sulphuric acid is then added to the contents of the flask, by means of the funnel-tube, to cause the evolution of a moderate stream of sulphuretted hydrogen; this is conducted into the acidulated arsenical solution, contained in a test-tube or any convenient vessel. When the quantity of material to be examined is very small, the apparatus illustrated in Fig. 7 may be employed. From very dilute solutions the precipitate does not separate until the excess of the reagent added is expelled by a gentle heat or by exposure to the air. In all cases a gentle heat hastens the complete separation of the precipitate.

FIG. 7.



Apparatus for detecting arsenic by sulphuretted hydrogen.

Arsenious sulphide is insoluble in cold hydrochloric acid, and only very slightly soluble in the boiling concentrated acid; hot nitric acid decomposes and dissolves it to *arsenic acid*. It is readily soluble, to a colorless solution, in the caustic alkalies, and in the alkali sulphides and carbonates.

When *ten grains* of a pure aqueous solution of arsenious oxide are placed in a small test-tube, acidulated with two drops of hydrochloric acid, and treated with a slow stream of the washed sulphuretted gas, the following results are obtained.

1. 1–100th solution (1–10th grain of arsenious oxide) yields a very copious, bright yellow precipitate, which remains amorphous.
2. 1–1000th solution : an immediate precipitate, which very soon becomes quite copious.
3. 1–10,000th solution : an immediate yellow turbidity ; if the mixture, after being saturated with the gas, be allowed to stand at the ordinary temperature for several minutes, quite good yellow flakes appear, and these after a time fall to a very good deposit. If the mixture be heated, the precipitate separates almost immediately.
4. 1–25,000th solution : very soon a yellow turbidity ; after standing about ten minutes yellow flakes are just perceptible ; and after a few hours there is a quite satisfactory deposit. If after

the introduction of the gas the mixture be heated, the deposit appears within a very few minutes.

5. 1–50,000th solution: after a little time a perceptible yellowish turbidity; in about an hour distinct flakes appear suspended in the liquid, but their color is not satisfactory; after a few hours they assume a distinct yellow hue, but still remain suspended in the fluid, from which, however, they almost immediately separate on the application of heat.
6. 1–100,000th solution: after a few minutes the mixture presents a perceptible cloudiness; after several minutes a distinct turbidity and a just perceptible yellow tint; after a few hours distinct flakes appear, but their true color is not apparent; after thirty-six hours there is a quite distinct yellow deposit. *One hundred grains* of the solution yield in a little time a very perceptible yellowish turbidity; after a few hours a decided yellow deposit; in twenty-four hours the deposit is about the same as that from ten grains of a 1–10,000th solution which has stood the same length of time.

When *normal* solutions of the acid are treated with the reagent, they also yield arsenious sulphide; but under these conditions the arsenical sulphide, except when from concentrated solutions, entirely remains in solution, imparting a yellow color to the liquid. *Ten grains* of a 1–100th solution of this kind yield after a little time a quite good yellow precipitate; but the same quantity of a 1–1000th solution yields only an intensely yellow liquid; a 1-25,000th solution yields a quite distinct yellow coloration; and a 1–50,000th solution, after a little time, acquires a perceptible yellow tint. *Alkaline* solutions of the acid, even when highly concentrated, altogether fail to yield a precipitate when treated with the reagent.

The *limit* of the visible reaction of this test, when applied to acidulated solutions of the poison, has been variously stated by different observers. Thus, Lassaigne placed it, for solutions acidulated with hydrochloric acid, at one part of arsenious oxide in 80,000 parts of liquid; Reinsch, at one part in 90,000; Brandes, one part in 160,000; Devergie, one part in 500,000; and Horsley, at one part in 1,120,000 parts of fluid. Dr. Taylor states that the 1–400th of a grain of the poison in half an ounce of water produced a scarcely perceptible yellow tint. In this case the acid was present in something less than 100,000 parts of liquid.

As neither of these observers, except Dr. Taylor, states the *quantity* of solution operated upon, these discrepancies are easily reconciled. The effect of quantity is well illustrated under experiment 6, in which *ten grains* and *one hundred grains* respectively of the same solution were employed. Here it will be observed that although the degree of dilution was the same, yet the absolute quantity of arsenic in one case was ten times greater than in the other, and the results differed correspondingly. It is obvious that a similar difference would be observed between different quantities of any other solution, until the degree of dilution equalled the solubility of the arsenious sulphide, when no quantity, however great, would yield a precipitate.

Confirmation of the Precipitate.—The arsenical nature of arsenious sulphide may be established by either of the following methods:

1. When the hydrochloric acid mixture containing the precipitate is boiled with a slip of bright copper-foil, the sulphide is decomposed with the deposition of metallic arsenic upon the copper; if the coated copper be then washed, dried, and heated in a reduction-tube, the metallic arsenic is volatilized and yields a sublimate of octahedral crystals of arsenious oxide. In this manner the nature of the precipitate from even less than the 1–1000th of a grain of the poison may be fully established.

2. When arsenious sulphide is dissolved in a few drops of hot nitric acid, the solution cautiously evaporated to dryness, and the dry residue treated with a few drops of a strong solution of silver nitrate, it assumes a brick-red color, due to the formation of silver arsenate.

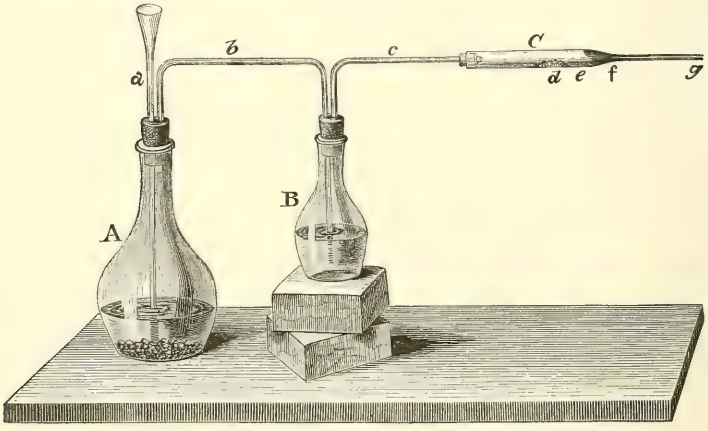
3. When washed, dried, and heated in a reduction-tube, the arsenical sulphide readily fuses to an orange-colored mass, then entirely volatilizes, yielding a sublimate, the lower portion of which generally has an orange-red color and consists of microscopic globules or drops; the upper part of the sublimate has a yellow color, and its upper margin contains crystals of arsenious oxide. Small precipitates of the sulphide are most readily recovered, as recommended by Devergie, by collecting them on a small filter, dissolving in ammonia, and evaporating the solution at a gentle heat to dryness, in a watch-glass, when the sulphide remains as a yellow residue.

4. When the dried precipitate is mixed with several times its volume of well-dried potassium ferrocyanide, or of a thoroughly dried mixture of one part of potassium cyanide and three parts of

sodium carbonate, and heated in a reduction-tube, it undergoes decomposition, with the production of a sublimate of metallic arsenic. If this operation be performed in a reduction-tube having a narrowly contracted neck, the precipitate from the 1–1000th of a grain of arsenious oxide will yield very satisfactory results. According to M. Gautier, this method is attended with loss of arsenic, yielding only twenty-nine out of thirty-six parts. (*Ann. d'Hyg.*, Jan. 1876, 153.)

For the reduction of arsenious sulphide by a mixture of potassium cyanide and sodium carbonate, Fresenius and Babo recommend to heat the arsenical mixture in an atmosphere of dry carbon dioxide, commonly known as carbonic acid gas. For this purpose they employ the apparatus illustrated in Fig. 8.

Fig. 8.



Fresenius and Babo's apparatus for the reduction of arsenious sulphide.

The flask A is charged with a mixture of water and lumps of solid marble, and sufficient hydrochloric acid added, through the funnel-tube *a*, to evolve a moderate stream of the gas; this is conducted by means of the tube *b* into strong sulphuric acid contained in the flask B, where it is thoroughly dried; the tube *c* conducts the dried gas into the reduction-tube C, in which is placed the arsenical mixture *d*. When the apparatus is filled with the gas, the tube C is heated in its whole length very gently until the contained mixture is quite dry; when every trace of moisture is expelled, and the stream of gas has become so slow that the single bubbles pass through

the sulphuric acid in B at intervals of about one second, the reduction-tube is heated to redness at the point *e* by means of a spirit-lamp; when *e* is red-hot, the flame of another lamp is applied to the mixture, proceeding from *b* to *e*, until the whole of the arsenic is expelled. The far greater portion of the volatilized arsenic recondenses at *f*, while a small portion escapes through *g*, imparting to the surrounding air a peculiar garlic-like odor. By slowly advancing the flame of the second lamp up to *f*, the whole of the condensed arsenic collects in the narrow neck of the tube. The authors of this process state that it will yield a perfectly distinct metallic mirror from the 1–300th of a grain of arsenious sulphide.

Fallacies.—The only metal besides arsenic with which sulphuretted hydrogen produces a bright yellow precipitate is *cadmium.* But, as the sulphide of arsenic when precipitated from organic solutions may have only a dull yellow color, it is important to bear in mind that certain other metallic sulphides, either in their pure state or when mixed with organic matter, may also present a similar appearance. The only substances that under any circumstance could thus be confounded with arsenic are cadmium, selenium, tin, and antimony. The sulphides of these substances possess the following properties:

1. The sulphide of *cadmium* is thrown down by the reagent from moderately acid solutions of the salts of the metal, but *strongly* acidulated solutions fail to yield a precipitate. The precipitate is readily decomposed and *dissolved* by hydrochloric acid; so, also, unlike arsenious sulphide, it is *insoluble* in the alkalies and their sulphides, and it is, therefore, produced in solutions containing a free alkali. When boiled with copper-foil in water acidulated with hydrochloric acid, it fails to produce a deposit upon the copper. Fused in a reduction-tube with a reducing agent, it yields a metallic sublimate, which, however, in its physical appearance is very unlike the arsenical deposit, and which when resublimed in the open tube fails to yield octahedral crystals.

2. Acidulated solutions of *selenious* acid yield with sulphuretted hydrogen a precipitate of selenium sulphide, which at first has a yellow color, but soon changes to reddish-yellow, and finally to *orange-red.* In dilute solutions the precipitate may remain suspended for some time, and present a yellow appearance, much like the arsenical compound; but after a time it separates of its charac-

teristic color. The same precipitate separates from neutral and alkaline solutions. The precipitate, like the arsenical sulphide, is insoluble in hydrochloric acid, even on the application of heat. Unlike the arsenical compound, however, it is wholly *insoluble* in ammonia. It also fails to yield a metallic deposit when boiled with diluted hydrochloric acid and copper-foil. When fused with a reducing agent in a reduction-tube, it yields a sublimate which may resemble somewhat that produced by arsenic, but the deposit fails to yield octahedral crystals upon resublimation.

3. Per-combinations of *tin*, or *stannic* compounds, yield with the reagent from acidulated solutions a precipitate of stannic sulphide, SnS_2, the color of which in the moist state somewhat resembles that of sulphide of arsenic, but when dried it has a very dull yellow color. The same precipitate separates from neutral, but not from alkaline, solutions. The precipitate is slowly soluble in cold hydrochloric acid, but readily in the hot concentrated acid. It is very sparingly soluble in ammonia, but readily soluble in potassium hydrate. When boiled with water containing hydrochloric acid and a slip of copper-foil, it may impart to the latter a slight stain, but when the stained metal is heated in a reduction-tube it fails to yield a crystalline sublimate. The precipitate also fails to yield a metallic sublimate when heated in a reduction-tube with a reducing agent.

4. The sulphides of *antimony*, as thrown down from pure acidulated solutions by sulphuretted hydrogen, have an *orange-red* color; the same precipitates are partially deposited in neutral and alkaline solutions of the metal. The precipitates, unlike the arsenious sulphide, are *soluble* in cold concentrated hydrochloric acid, and nearly wholly *insoluble* in ammonia; they are readily soluble in potassium hydrate. When boiled with diluted hydrochloric acid and copper-foil, they impart to the latter a metallic coating, which usually has a violet color; when the coated copper is heated in a reduction-tube, it generally fails to yield octahedral crystals. (See *post*, 275.) Nor will the precipitates when heated in a reduction-tube with a reducing agent yield a metallic sublimate.

As a source of fallacy of the sulphur test, it has been claimed that if the iron sulphide contains metallic iron, as is frequently the case, and the iron salt or the acid employed for its decomposition is contaminated with arsenic, the nascent hydrogen evolved by the

metallic iron will convert the arsenic, in part at least, into arsenuretted hydrogen, which may carry the metal over into the solution being tested for arsenic. This, however, is an error. In repeated experiments with impure materials of this kind, we have failed to find the least trace of arsenic evolved from the mixture.

Thus, when a mixture of 50 grammes each of iron sulphide and metallic iron was treated in a flask with 100 c.c. of diluted sulphuric acid containing one gramme of arsenious oxide, added small portions at a time, and the washed evolved gas conducted into 100 c.c. of warmed nitric acid of sp. gr. 1.40, which readily decomposes both sulphuretted hydrogen and arsenuretted hydrogen, not a trace of arsenic was found in the nitric acid residue, when most carefully examined by Marsh's apparatus. Any arsenic present in the material employed for generating the sulphuretted hydrogen is immediately converted into arsenious sulphide, and remains as such in the generating flask, the sulphide not being decomposed by nascent hydrogen.

4. *Reinsch's Test.*

When a solution of free arsenious acid or of an arsenite is strongly acidulated with hydrochloric acid, and the mixture boiled with bright metallic copper, the latter decomposes the arsenical compound and receives a coating of metallic arsenic. This fact was first observed, in 1843, by Reinsch; but Dr. Taylor was the first to apply it as a test in medico-legal investigations. The proportion of hydrochloric acid employed should form about one-eighth of the volume of the arsenical solution; without the addition of the acid the metal is not deposited. The copper may be employed in the form either of fine wire or of very thin foil; the latter, however, is preferable. It is essential that the copper have a bright surface: this is readily effected by means of a fine file or of sand-paper. The color of the metallic deposit will depend much upon the thickness of the latter: when quite thin, it presents a bluish or violet appearance, but when comparatively thick, it has a steel-like or iron-gray color. When the metallic coating is very thick, continued boiling causes it to separate from the copper, in the form of grayish or black scales.

This deposit is not, as was formerly supposed, pure metallic arsenic, but a combination of this metal and copper. M. Lippert maintains that it has a constant composition, being a definite alloy, consisting of 32 per cent. of arsenic and 68 per cent. of copper, its

formula being Cu_5As_2. The large proportion of copper contained by the deposit adds very much to the delicacy of the test. This reaction will serve to withdraw the whole of the arsenic from solutions of arsenious acid and of arsenites; but when the metal exists in the form of *arsenic acid*, it is deposited only from somewhat strong solutions.

The arsenical nature of the deposit may be shown in the following manner: the coated copper, after being carefully washed with pure water and dried in a water-bath, is heated by means of a spirit-lamp in a narrow, perfectly dry and clean reduction-tube, when the arsenic volatilizes, and, becoming oxidized, yields a sublimate of octahedral crystals of arsenious oxide. This sublimate usually forms within from a quarter to half an inch above the point at which the heat is applied. When the sublimate is not exceedingly minute, it presents a well-defined ring of sparkling crystals to the naked eye. Under the microscope, these crystals present the appearances illustrated in Plate IV., fig. 5. The absolute size of the crystals will depend somewhat upon the quantity of the metal present, as well as upon the diameter of the reduction-tube. The portion of the tube containing the sublimate may be separated with a file, boiled in a very small quantity of water, and the solution examined by the ammonio silver nitrate or any of the other tests for arsenious acid.

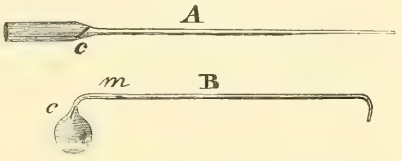
When *one grain* of a pure aqueous solution of arsenious oxide is acidulated with pure hydrochloric acid, and the mixture heated in a thin watch-glass with a small fragment of bright copper-foil, it yields the following results.

1. $\frac{1}{100}$ grain of arsenious oxide yields a copious, iron-gray deposit, which when heated in a narrow reduction-tube furnishes a very good sublimate, consisting of innumerable octahedral crystals.
2. $\frac{1}{1000}$ grain yields a good, steel-like deposit, which when sublimed in a reduction-tube yields results similar to 1, only that the crystals are generally somewhat smaller.
3. $\frac{1}{10,000}$ grain: as soon as the mixture is heated to the boiling temperature the copper shows a distinct deposit, which in a little time becomes quite satisfactory; when this is volatilized in a very narrow reduction-tube, it yields a sublimate which is visible to the naked eye, and which under the microscope is very satisfactory.

When deposits smaller than the one just mentioned are heated in

a reduction-tube of the ordinary form, even of very narrow bore, the results are not uniform, owing to the fact that the sublimate is distributed over a comparatively large space, and part of it seems entirely to escape condensation, at least in the lower portion of the tube. With such deposits, however, very uniform results may be obtained by the following method. A thin, perfectly clean and dry tube, of about the 1–10th of an inch in diameter, is drawn out into a capillary neck having an internal bore of about the 1–40th of an inch, as illustrated in Fig. 9, A. The coated copper is then introduced through the wider portion of the tube to the point *c*, and the neck of the tube at a little distance above the copper is moistened with water or wrapped with wet cotton. The wide end of the tube is then cautiously fused shut by a very small blow-pipe flame, and the fusion slowly advanced to the point occupied by the copper, as shown in B. The capillary end may now be fused shut. When wiped and examined by the microscope, the arsenical sublimate will be found at about the point *m*, forming a very narrow ring of octahedral crystals. As these tubes may readily be formed with walls less than the 1–100th of an inch in thickness, they permit the application of the higher powers of the microscope. They may be reserved for future examination; after a time, however, the sublimate deteriorates somewhat, and it may even, if the deposit is very small, wholly disappear.

FIG. 9.



Tubes for sublimation of arsenic. Natural size.

4. $\frac{1}{25,000}$ grain: when a fragment of copper-foil measuring about 1–10th by 1–20th inch is employed, and the mixture kept at a boiling heat for some time, with renewal of the evaporated fluid by pure water, the copper acquires a decided steel-like coating; when this is sublimed in a tube of the form described above, it yields to the naked eye a visible mist, which under an amplification of seventy-five diameters is found to consist of many hundreds of well-defined octahedral crystals. In a number of instances over one hundred crystals, varying in size from the 1–2000th to the 1–8000th of an inch in diameter, were counted in a single field of a two-thirds inch objective, without change of

focus; most of the crystals measured about the 1–4000th of an inch in diameter.

5. $\frac{1}{50,000}$ grain, when treated for some minutes as under 4, imparts to the copper a distinct steel-like tarnish, which when volatilized, in the manner described above, yields a very satisfactory microscopic sublimate. In many instances over fifty crystals, measuring from the 1–3000th to the 1–10,000th of an inch in diameter, were counted in a single field of the objective. So far as the evidence of the presence of octahedral crystals is concerned, this sublimate, under the microscope, is as satisfactory as that from the 1–100th of a grain or larger quantity of arsenious oxide, the only difference being in the size and number of the crystals.

6. $\frac{1}{100,000}$ grain: the copper receives a very slight tarnish, which when volatilized sometimes yields a satisfactory crystalline sublimate; but frequently the crystals are so minute that their angular nature cannot be satisfactorily determined.

For the examination of these sublimates a magnifying power of about seventy-five diameters is generally the most useful. Under this amplification, the angular nature of a crystal measuring the 1–5000th of an inch in diameter is perfectly distinct and satisfactory: the weight of such a crystal would not exceed the 1–200,000,000th of a grain. Under the same power, a crystal measuring the 1–10,000th of an inch appears only as a distinct point; but with a power of one hundred and fifty, its angular form may be distinctly recognized: its weight would be less than the 1–1,000,000,000th of a grain. On account of the curvature of the glass tube, crystals but little less in size than the last mentioned are not easily determined, even with the higher powers of the microscope. It is not, of course, intended to imply that quantities of the poison in themselves as small as those just mentioned could be recovered from a solution and reproduced in the crystalline form; but only that these crystals may thus be recognized and identified when they form separate portions of a sublimate. The least quantity of the poison that will furnish these crystals, even with the greatest care and under the most favorable circumstances, according to the above method, is about the 1–50,000th of a grain.

Various and very discordant limits have been assigned to this test by different observers. However, as these experimentalists only state the degree of dilution, without mentioning either the quantity

of solution examined, the size of the copper, or the diameter of the reduction-tube employed, these discrepancies are readily explained.

Fallacies.—The production of a sublimate of octahedral crystals by this test is quite characteristic of arsenic. Various other metals, however, as antimony, mercury, silver, bismuth, platinum, palladium, and gold, are deposited upon copper under the same conditions as arsenic. Tin may also impart a slight stain to the copper; so, also, organic matter, especially if it contain sulphur; and the prolonged action of boiling hydrochloric acid alone may produce a distinct tarnish. The antimonial deposit has usually a peculiar violet color, while the deposits from mercury, silver, and bismuth have generally a bright silvery appearance, and that from gold a yellow hue. Under certain circumstances, however, most of these deposits may closely resemble that from arsenic. The platinum and palladium deposits present an appearance very similar to that of the arsenical coating.

Of these various metallic deposits, the only ones which, when heated in a reduction-tube, will, like arsenic, volatilize and yield a sublimate, are *mercury* and *antimony*. But the sublimate from mercury consists of opaque spherical globules, which, when viewed under incident light with the microscope, have a bright silvery appearance; and that from antimony is usually either amorphous or at most granular: both these sublimates, unlike that from arsenic, are insoluble in water.

We have elsewhere shown (*Amer. Jour. Med. Sci.*, Oct. 1877, 399) that the antimonial sublimate *may* contain octahedral crystals, at least when a comparatively large deposit is heated. But the antimony deposit requires a much higher temperature than arsenic for its vaporization, and, being less volatile, the sublimate is very near or only slightly in advance of the copper slip. Moreover, under the microscope, any crystals, if present, will be found in the lower margin of the deposit and mixed more or less with amorphous or granular matter. Sometimes, though rarely, the antimony sublimate contains crystalline needles. In this connection it should be remembered that commercial tartar emetic sometimes contains sufficient arsenic, as an impurity, to yield in this manner a very distinct sublimate of octahedral crystals in advance of the antimonial deposit.

A deposit of *organic* matter upon the copper may also give rise to a sublimate, but this is amorphous, and its true nature is at once revealed by the microscope. When very complex organic mixtures

strongly acidulated with hydrochloric acid are boiled for some time in contact with metallic copper, the metal may present a very distinct stain, and yield an amorphous sublimate which sometimes contains small acicular crystals, consisting apparently of a compound of copper. This sublimate deposits very near the copper, and is not resublimed upon the further application of heat.

If *sulphur* in certain states of combination, especially as *sulphurous acid* or an alkaline sulphite, be present in the liquid, the copper will receive a deposit or coating very similar in appearance to that produced by arsenic in certain quantity. After a time the deposit may become detached in metal-like flakes, which have, as we have found, the composition Cu_2S. When the coated copper is heated in a tube, a portion of the sulphur may be volatilized and yield a sublimate of minute globules which in certain respects may closely resemble an arsenical sublimate, but readily distinguished from it in not being crystalline. When, therefore, sulphurous acid is employed as a reducing agent in the preparation of a liquid for testing, it should be wholly expelled before the application of this test.

Finally, if the copper-foil or the reduction-tube is not perfectly dry, the moisture may condense in the form of a mist-like deposit at about the point at which the arsenical sublimate usually forms; but the true nature of this deposit also is at once revealed by the microscope.

From what has now been stated, it is obvious that the presence of arsenic is not fully established until the coated copper yields a sublimate of well-defined octahedral crystals. In applying this confirmatory reaction, however, it should be borne in mind that when a comparatively large arsenical deposit is heated in a very small reduction-tube the sublimate may consist alone of granules, or a portion of the arsenic may even deposit in its metallic state. It rarely happens, however, that at least the upper margin of an arsenical sublimate does not contain the characteristic crystals. Should there be any doubt as to the nature of the sublimate, the lower end of the tube may be removed and the deposit resublimed, when, if consisting of arsenic, it will be converted into the crystalline form. In all cases the size of the reduction-tube should be in suitable proportion to the quantity of deposit to be examined.

But even should this test, when applied to a suspected solution, yield an arsenical sublimate, it of course would not follow that the

poison was really derived from the suspected liquid, unless the analyst was perfectly certain of the purity of the hydrochloric acid, and in some instances also of the copper, employed. As found in commerce, hydrochloric acid may contain very notable quantities of arsenic. In all cases a portion of the sample of the acid about to be employed should first be diluted with five or six volumes of water and boiled for about ten minutes with a slip of bright copper; if this fails to yield a deposit, the acid may be considered free from arsenic. In regard to the purity of copper, it is now known, chiefly through the researches of Dr. Taylor, that this metal, as usually employed in investigations of this kind, nearly always contains traces of arsenic. This impurity, however, could only lead to error when the copper is acted upon and dissolved by the liquid with which it is boiled; any arsenic thus dissolved might then deposit upon a fresh portion of the copper. This objection, therefore, has no practical force, except in cases in which a very notable quantity of the copper has dissolved and only a very minute trace of arsenic has been detected. When, in the application of the test to a suspected solution, the copper promptly receives an arsenical deposit, which after the addition of successive slips of the metal ceases to take place, it is quite certain that the poison is not derived from the copper.

For the detection of traces of arsenic in copper we have found the following method, first advised by F. Field (*Chem. Gaz.*, 1857, 313), exceedingly delicate. Ten grains of the copper are dissolved in slight excess of pure, hot nitric acid, the solution diluted to about three ounces of fluid, and ammonia added until the oxide of copper is precipitated, but not redissolved; the precipitate is then redissolved by the addition of about twenty-five grains of ammonium oxalate, the copper oxalate thus produced precipitated by slight excess of hydrochloric acid, and the mixture allowed to stand some hours. The solution is then filtered, the filtrate saturated with sulphurous acid gas, concentrated to a small volume, and tested for arsenic, either by sulphuretted hydrogen or by a fresh piece of copper.

For this same purpose Dr. Odling recommends (*Jour. Chem. Soc.*, July, 1863, 248) to distil a few grains of the copper, cut into small pieces, with an excess of pure hydrochloric acid and ferric chloride, the distillation being carried to dryness: the dry residue may be redistilled with a little fresh hydrochloric acid. By this

treatment the copper is quickly dissolved, and any arsenic present converted into chloride and thus carried over with the distillate. The distillate is tested for arsenic in the usual manner. Ferric chloride, Dr. Odling adds, may be purified from arsenic by evaporating it once or twice to dryness with excess of hydrochloric acid.

Interferences.—Should this test fail to yield a metallic deposit upon the copper, it would not follow from this fact alone that arsenic was entirely absent, even as arsenious acid, since the deposition of the metal may be prevented by the presence of certain other substances. Thus, in even strong solutions of the poison containing only a small quantity of a *chlorate,* as potassium chlorate, the copper remains perfectly bright, but the liquid acquires a bluish or greenish-blue color, due to the formation of a soluble salt of copper. Should arsenic and a chlorate occur in the same mixture, the solution is cautiously evaporated to dryness, and the dry residue fused in a long, narrow glass tube until the evolution of oxygen ceases: by this operation the chlorate will be converted into a chloride, and the arsenic into *arsenic oxide.* The tube is then cut into small pieces and boiled with a small quantity of pure water until the saline matter has entirely dissolved, and the solution thus obtained, after filtration if necessary, is saturated with sulphurous acid gas, the excess of which is afterward expelled by a gentle heat. The solution, which now contains the arsenic as arsenious acid, together with the chloride resulting from the decomposition of the chlorate, may be acidulated with hydrochloric acid and examined in the usual manner.

So, also, the presence of *manganese dinoxide,* and of other substances that decompose hydrochloric acid with the elimination of free chlorine, may interfere with the reaction of the test. And the same is true of free nitric acid. This acid, however, has little action upon the test unless present in quite notable quantity or the solution be concentrated to a small volume, when it acts upon and dissolves the copper. In case of the presence of free nitric acid, the solution may be neutralized with potassium hydrate, then acidulated with hydrochloric acid, and tested as usual; or the solution may be cautiously evaporated to dryness, the residue dissolved in water, this solution saturated with sulphurous acid gas, then gently heated to expel the excess of gas, and examined.

The alkaline *nitrates* have little or no effect upon the test until the solution is evaporated to near dryness, when they cause the solu-

tion of the copper. In a mixture containing the 1–5th of its weight of potassium nitrate and 1–500th of arsenious oxide, the reaction takes place much the same as in a pure solution of the oxide.

In conclusion, it may be remarked that this method of Reinsch possesses several advantages which entitle it to more consideration than it has usually received at the hands of chemists. Thus, it is easily and quickly applied, requiring but little apparatus, and that of the most simple kind; it usually requires the purity of only one substance, namely, the hydrochloric acid, to be known, and this is readily established by means of the test itself; it requires no dilution of the suspected liquid, but, on the contrary, permits its concentration to almost any extent while the test is being applied; it may be applied directly to much more complex organic mixtures than either of the other tests for this poison; and, finally, it serves to separate from complex mixtures and reproduce in an unequivocal form a less quantity of the poison than any other known test, except, perhaps, one of the methods of Marsh's process, with which, however, it is about equally delicate.

5. *Marsh's Test.*

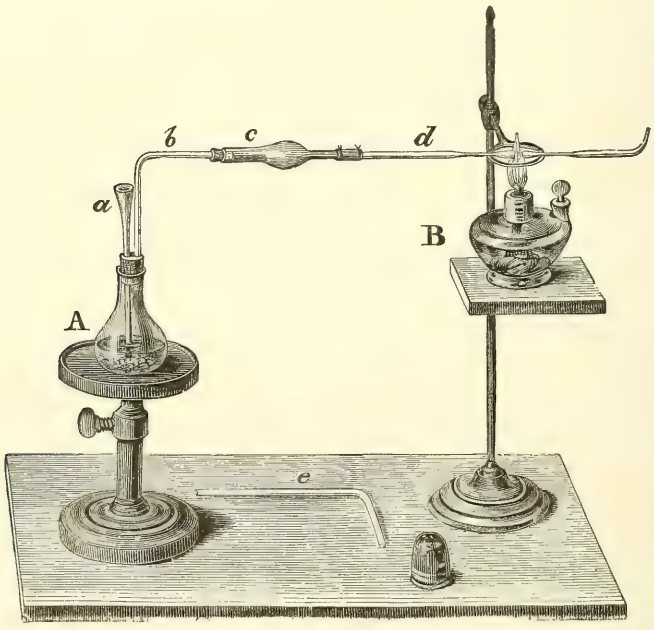
When metallic zinc is treated with diluted sulphuric acid, the hydrogen of the latter is displaced by the metal with the formation of zinc sulphate, the hydrogen displaced passing off in its free state: $Zn + H_2SO_4 = ZnSO_4 + H_2$. If, however, arsenious acid or arsenic acid or any of the soluble compounds of the metal be present, the nascent hydrogen decomposes the arsenical compound, and, uniting with the metal, forms *arsenuretted hydrogen* gas, AsH_3, which is evolved in its free state. The reaction in the case of arsenious acid is as follows: $3Zn + 3H_2SO_4 + H_3AsO_3 = 3ZnSO_4 + 3H_2O + AsH_3$; with arsenic acid: $4Zn + 4H_2SO_4 + H_3AsO_4 = 4ZnSO_4 + 4H_2O + AsH_3$. When the arsenic is present as a chloride, it yields hydrochloric acid and the arsenuretted gas. Neither metallic arsenic nor the sulphides of the metal will yield a trace of the gas. The production of arsenuretted hydrogen, under these conditions, has long been known, but Mr. Marsh, of Woolwich, in 1836, was the first to employ it as a method for the detection of arsenic.

Arsenuretted hydrogen is a colorless, extremely poisonous gas, having a peculiar alliaceous odor, and specific gravity of 2.695; it is neutral in its reaction, and but sparingly soluble in water. It burns

with a bluish flame, giving rise to arsenious oxide, and is readily decomposed by heat into free hydrogen and metallic arsenic; it is also readily decomposed by solutions of the easily reducible metallic oxides. These properties serve, in the manner to be pointed out hereafter, for the detection of very minute traces of the gas.

Various forms of apparatus have been proposed for the production of this gas in its application to the detection of arsenic, but the most efficient is that advised by Otto, as illustrated, in principle, by Fig. 10. The gas-flask A, which may be substituted by a sim-

Fig. 10.



Apparatus for the application of Marsh's test.

ple wide-mouthed bottle or in delicate experiments by a long test-tube, is provided with a closely-fitting cork carrying the funnel-tube *a* and the exit-tube *b*; this tube should be tolerably wide, and have its lower end cut obliquely, to facilitate the dropping back of any condensed liquid into the flask. *c* is a drying-tube containing fragments of potassium hydrate or of calcium chloride, kept in their place by loose cotton. Unless the experiment is to be continued for some time, it is only necessary to fill the drying-tube loosely with asbestos

moistened with concentrated sulphuric acid. This tube is connected with the tube *b* by means of a perforated cork, and with the reduction-tube *d* by a short india-rubber tube. The reduction-tube (*d*) should be of hard glass, free from lead, and have an internal diameter of about 3–20ths of an inch, and walls not less than the 1–20th of an inch in thickness; its outer portion should be contracted in two or three places, as shown in the figure, and terminate in a turned-up, drawn-out point, which is fused in a small flame of a spirit-lamp until the opening becomes quite small. By preparing the end of the tube in this manner there is no danger of its fusing shut when the jet of gas is afterward ignited. In very delicate experiments, the bore of the contracted portions of the tube should not exceed the 1–20th of an inch in diameter. Several of these tubes should be prepared and at hand.

About two ounces, or sixty grammes, of pure zinc, either granulated or cut into very small pieces, are placed in the flask A, and, the apparatus being adjusted, covered with a cooled mixture consisting of one measure of pure concentrated sulphuric acid and four measures of distilled water, added through the funnel-tube *a*, which should extend to near the bottom of the flask. The zinc will now decompose the acid, with the evolution of hydrogen, in the manner before described. If the zinc should act only very slowly upon the acid, as is frequently the case with the pure metal, the action may be hastened by the addition of a few drops of platinic chloride. For this purpose, it is sometimes advised to add a little cupric sulphate; but, according to M. Gautier (*Ann. d'Hyg.*, Jan. 1876, 149), the addition of this salt is attended with the loss of arsenic.

Should the zinc or the sulphuric acid be contaminated with arsenic, this will give rise to arsenuretted hydrogen. Before, therefore, applying the test to a suspected solution, the purity of the materials employed must be fully established. For this purpose, after the apparatus has become completely filled with hydrogen and while the gas is still being evolved, the outer uncontracted portion of the reduction-tube is heated to redness, as illustrated in the figure, for about fifteen minutes or longer. If this fails to produce a metallic deposit or stain in the contracted part of the tube, in advance of the part heated, the material may be considered free from arsenic. The purity of the materials having been thus established, it may be

necessary to wash and renew the zinc, dry the tubes, and add a fresh portion of the diluted acid.

Sulphuric acid in its *concentrated* state should not be added to the zinc mixture, since, as first shown by H. Kolbe (*Ding. Poly. Jour.*, April, 1872, 160), and confirmed by our own experiments, if the undiluted acid be brought in contact with the metal in the presence of nascent hydrogen, it may be reduced with the formation of sulphuretted hydrogen, which might in part or wholly retain any arsenic present by converting it into arsenious sulphide. When the acid is diluted with about twice its volume of water this reduction does not take place.

The apparatus being adjusted and completely filled with evolved hydrogen, the jet of gas, as it issues from the drawn-out end of the reduction-tube, is ignited, care being taken not to apply a light until the whole of the atmospheric air is expelled from the apparatus, as otherwise an explosion might occur. A small quantity of the arsenical solution is then introduced into the funnel-tube, and washed into the flask by the subsequent addition of a few drops of the diluted sulphuric acid. The decomposition of the arsenical compound, with the evolution of arsenuretted hydrogen, will commence *immediately*. The presence of the arsenuretted gas may be established by three different methods,—namely: α. By the properties of the ignited jet; β. By decomposing it by heat applied to the reduction-tube; and, γ. By its action upon a solution of silver nitrate.

α. The ignited jet.—As soon as the arsenical solution is introduced into the flask the evolution of gas increases; this increase is quite perceptible even when the liquid within the flask contains only the 1–1,000,000th of its weight of arsenious oxide. The flame of the ignited jet will now increase in size, acquire a bluish tint, and, unless only a minute quantity of arsenic is present, evolve white fumes of arsenious oxide; so, also, sometimes, the flame emits a peculiar alliaceous odor. If the white fumes thus evolved be received upon a cold surface, as an inverted watch-glass, they condense to a white powder, which sometimes contains octahedral crystals. The arsenical nature of this powder may be shown by any of the methods heretofore pointed out for the recognition of solid arsenious oxide. This, however, is by no means a delicate method for detecting the presence of the arsenuretted gas; and it should never be employed to the exclusion of that now to be mentioned.

If the flame be allowed to strike against a cold body, as a piece of white porcelain held in a horizontal position, it yields a deposit of metallic arsenic on the cold surface. In experiments with very dilute solutions, the porcelain should be applied immediately after the introduction of the arsenical compound, since the evolution of the arsenuretted gas begins at once, and the whole of the metal may be thus rapidly evolved. As soon as a well-marked deposit is obtained on the porcelain, the position of the latter should be changed, so that the flame may strike upon a fresh surface: if it can be done, a number of these deposits should be collected upon several different pieces of the porcelain.

When the amount of arsenic present is not very minute, the central portion of the deposits thus obtained presents a bright steel-like appearance; this is surrounded by a darker and less lustrous portion, the outer margin of which has sometimes a brownish color. The exact appearance of these deposits, however, depends much upon the quantity of arsenic present, the character of the flame, and the position occupied by the porcelain: sometimes they consist simply of brownish stains, whilst at other times they are in the form of rings. From very dilute solutions they are produced only when the gas burns with a small, steady, round flame; when the supply of gas is so rapid as to produce a long, pointed flame, they are sometimes not obtained from even strong solutions of the metal. When the gas burns with a conical flame, the porcelain should be applied at about the centre of its upper third or still nearer its point; on the other hand, when the flame is short, full, and round, the cold surface should be held very near its base.

Delicacy of this method.—In investigating the limit of this test in regard to the production of metallic deposits on cold porcelain, a gas-flask of about three fluid-ounces capacity was employed, except when the entire quantity of fluid did not exceed one hundred grain-measures, when the flask was substituted by a test-tube, three-fourths of an inch in diameter and five inches long. For the examination of very minute quantities of arsenious oxide, or of any other soluble combination of the metal, a test-tube has an advantage over a flask, in that the arsenical solution can, by means of the funnel-tube, be brought in contact with the zinc and be thus decomposed before becoming much diffused through the diluted sulphuric acid.

1. $\frac{1}{1000}$ grain of arsenious oxide in solution in ten grains of water,

when added to an active apparatus containing something less than an ounce of pure zinc and *ninety grain-measures* of diluted sulphuric acid, yields in a few moments, from the ignited jet, metallic deposits, which continue to be formed until about sixty can be obtained, after which the evolved gas gives no evidence whatever of the presence of the metal. The degree of dilution in this case, providing the poison became equally diffused throughout the whole of the liquid in the apparatus, would be one part of arsenious oxide in 100,000 parts of the liquid mixture.

Of six experiments, in each of which the 1–1000th of a grain of arsenious oxide, in solution in ten grains of water, was added to an active apparatus containing *two hundred and ninety* grain-measures of diluted sulphuric acid,—the poison now forming only the 1–300,000th of the liquid mixture,—the highest number of well-defined deposits obtained was sixty-seven, the lowest fifty-two. If, therefore, none of the metallic arsenic escaped condensation,—which, however, is not the fact,—a single deposit could not on an average have represented more than the 1–60,000th of a grain of arsenious oxide, or only about the 1–80,000th of a grain of the metal; yet they each, with very few exceptions, measured from the 1–10th to the 1–14th of an inch in diameter. The size of these deposits will of course depend somewhat upon the size of the flame, which in its turn will depend upon the supply of gas and the orifice of the tube.

Experiments made with the same quantity of the poison in the presence of *five hundred* grains of liquid—or under a dilution of 500,000 parts of fluid—gave much the same results as those just described.

2. $\frac{1}{2500}$ grain of arsenious oxide, in an apparatus containing *one hundred* grains of liquid, or under a dilution of 250,000, furnished as the average of six experiments twenty-nine very satisfactory deposits.

The same quantity of the poison in *five hundred* grains of liquid, or under a dilution of 1,250,000, gave, in several experiments, several distinct stains, but in no instance were the results satisfactory.

3. $\frac{1}{5000}$ grain of arsenious oxide, in *one hundred* grains of fluid, or under a dilution of 500,000, usually yields several satisfactory deposits. But the same quantity of the oxide in *three hundred* grains of liquid failed in several instances to yield any satisfactory evidence of its presence.

The limit of this test, as applied in this manner, has been variously assigned; but, with few exceptions, the experimenters have stated only the degree of dilution of the solution, without mentioning the quantity employed. Thus, it has been stated that the method will yield satisfactory deposits when the solution contains only the 1–2,000,000th of its weight of arsenic. This is true, but it requires about one thousand grains of such a solution to furnish these results; the absolute quantity of the oxide present would therefore be about the 1–2000th of a grain. These statements have generally led to a misapprehension of the real delicacy of this test; and it has, therefore, in this respect been much overestimated. It is a fact that this method of Marsh, when referred to the mixture *within* the apparatus, will indicate the presence of the poison under a greater degree of dilution than any other known test; but at the same time it requires a much larger quantity of the solution for its application than will serve for either of the other tests.

From the experiments already cited, it would appear that when one hundred grains of liquid are employed—and this is about the smallest quantity that will evolve sufficient gas for the purpose—the least quantity of arsenious oxide that will yield satisfactory deposits is about the 1–5000th of a grain. This, therefore, so far as the production of deposits is concerned, is about the limit of the test. It has generally been conceded that this method would reveal the presence of a smaller quantity of arsenic than could be recovered by the method of Reinsch; but this is not the fact, since the latter process, in the manner already described, will serve to detect a much less quantity of the poison than can be made to reveal any evidence of its presence by at least this part of the method of Marsh.

Fallacies.—Solutions of antimony, under these same conditions, undergo decomposition with the production of *antimonuretted hydrogen*, which, like arsenuretted hydrogen, burns with the evolution of white fumes, and yields metallic deposits upon cold surfaces applied to the flame. It, however, unlike the arsenuretted gas, is destitute of odor, and burns with a greenish flame; moreover, when the white fumes evolved are condensed on a cold body, they yield an amorphous deposit, which is insoluble in water, and immediately assumes an orange-red color when moistened with a solution of ammonium sulphide; whilst that obtained from arsenic, under similar circumstances,

is soluble in water, and undergoes no immediate change when treated with ammonium sulphide.

The metallic deposits produced by antimonuretted hydrogen upon a piece of cold porcelain are usually destitute of lustre, and have a much darker color than those obtained from arsenic. These characters readily serve to distinguish between comparatively thick crusts of these metals; but in very thin deposits they may be entirely lost. The deposits of the two metals, however, differ greatly in regard to their chemical properties. 1. The arsenical crusts, except when very thin, are only very slowly soluble in a drop or two of a yellow solution of ammonium sulphide; whilst the antimonial deposits are readily soluble in this reagent. When the ammoniacal solution is evaporated to dryness on a water-bath, the arsenic remains as a *bright yellow* deposit of arsenious sulphide, which is readily soluble in ammonia, but insoluble in hydrochloric acid; under the same conditions antimony yields an *orange-red* residue, of antimonious sulphide, which is *insoluble* in ammonia, but readily *soluble* in concentrated hydrochloric acid. This method will serve for the discrimination of very minute deposits of the metals. 2. The spots produced by arsenic are readily soluble in a solution of either sodium or calcium hypochlorite; whereas those from antimony are insoluble, or dissolve only after prolonged digestion, in a solution of this kind. 3. The deposits from both metals readily dissolve in a drop of warm *nitric acid*, and yield, on the cautious evaporation of the liquid, a white residue. When, however, the arsenical residue is touched with a drop of a solution of silver nitrate, it assumes a brick-red color; whilst that from antimony remains unchanged. Various other methods have been proposed for distinguishing between these stains, but in point of delicacy they are much inferior to those already described.

Besides this fallacy of antimony, it has been objected that organic matter, certain combinations of iron, phosphorus, and sulphur, may under the above conditions yield stains somewhat similar to those produced by arsenic. But neither of these substances will yield a succession of spots; nor will either of them yield a single stain having the properties described under either of the three methods just mentioned for the identification of the arsenical deposit. In experiments for the purpose with mixtures containing iron, phosphorus, and sulphur, we have failed to obtain any stain whatever having the most remote resemblance to that produced by arsenic; nor, in numer-

ous applications of the test to animal and vegetable mixtures, have we ever found it to yield an organic stain.

β. Decomposition of the gas by heat.—As originally proposed by Marsh, this test consisted simply in obtaining metallic deposits from the ignited jet of gas, as now described. Berzelius was perhaps the first to resort to the decomposition of the arsenuretted gas by heat, as a means of its detection. The apparatus being filled with hydrogen and the evolution of gas quite moderate, heat is applied to the reduction-tube at a point about one-half or three-quarters of an inch on the inside of the outer contraction. When the part of the tube to which the flame is applied is quite red hot, a very small quantity of the arsenical solution is introduced, by means of the funnel-tube, into the flask. The arsenuretted hydrogen now evolved, as it passes through the red-hot portion of the reduction-tube, will be decomposed, with the production of a deposit of metallic arsenic in the contracted part, in advance of the flame. After a good deposit has thus formed, the heat of the lamp may be so changed that the metal may be deposited in the second contracted portion of the tube.

The physical appearance of the deposits thus obtained depends somewhat upon the quantity of arsenic present, but they usually, especially when obtained from very dilute solutions, consist of three conjoined portions, the inner of which is transparent and of a brown color, while the central part has a brilliant metallic appearance, and this fades into a lighter-colored or gray portion, which is imperceptibly lost. Very thick deposits may present much the same characters as presented by the sublimed metal already described. When the quantity of arsenic present is comparatively large and the current of gas rapid, sometimes arsenical stains may be obtained from the ignited jet at the same time that a deposit is being formed in the heated tube.

Delicacy of this method.—A much smaller quantity of the metal will yield deposits by this process than will serve for its detection from the ignited arsenuretted gas. This difference is due to the fact that by the method under consideration the metal eliminated from the decomposed gas may be collected at about the same point for several minutes, or longer if necessary; whereas from the gas when ignited it can be collected at the same place for only a few moments. Another advantage of this method over the preceding is, that it may

be applied with a less quantity of liquid, since it requires only a feeble current of gas. In the following experiments, one hundred grain-measures of liquid, including the arsenical solution, were present in the apparatus, and the reduction-tube was contracted to a bore of about the 1–20th of an inch in diameter. The arsenious oxide, as introduced in the apparatus, was in solution in ten grains of water.

1. $\frac{1}{2500}$ grain of arsenious oxide, in one hundred grains of liquid, or one part of the acid in the presence of 250,000 parts of fluid, yields in a very little time a very fine deposit, the inner portion of which has a brown color, while the outer part has a bright, metallic lustre.
2. $\frac{1}{5000}$ grain, under a dilution of 500,000 parts of liquid, yields much the same results as 1.
3. $\frac{1}{10,000}$ grain, under a dilution of 1,000,000, yields a quite good deposit.
4. $\frac{1}{25,000}$ grain, under a dilution of 2,500,000, yields after some minutes a very satisfactory deposit.
5. $\frac{1}{50,000}$ grain, in the presence of 5,000,000 parts of liquid, yields after several minutes a very distinct stain, the outer part of which has a dark, metallic appearance, and the inner, a brownish color.

In regard to the delicacy of this method, it may be remarked that in the whole range of chemical tests there is perhaps no other that will indicate the presence of a substance under as great a degree of dilution.

Fallacies.—Antimonuretted hydrogen also is decomposed under the above conditions, with the deposition of metallic antimony. Since, however, antimonuretted hydrogen is decomposed at a lower temperature than the arsenuretted gas, the antimony eliminated is always, in part at least and from dilute solutions wholly, deposited *before* reaching the part of the reduction-tube to which the flame is applied; when it yields deposits on both sides of the flame, the outer one is quite near the flame. On the other hand, arsenic deposits about one-half or three-quarters of an inch in advance, or on the *outer side* of the flame, and never before reaching the part of the tube to which the heat is directly applied. This difference in itself is quite sufficient to distinguish between these metals, when only one of them is present. Again, the arsenical deposit has usually a bright, metallic lustre, whilst the antimonial has a dull and darker appearance.

Very thin deposits of the two metals, however, may present very similar appearances.

In regard to the action of heat and chemical reagents upon these metallic deposits, they differ in the following respects:

a. If the tube, removed from the apparatus, be heated at a little distance from and on the inner side of the crust, and the heat then slowly advanced to it, the *arsenical* deposit readily volatilizes and recondenses a little farther on, in the form of brilliant, octahedral crystals of arsenious oxide. Under the same circumstances, the *antimonial* deposit requires a much higher temperature for its vaporization, and re-deposits quite near the point at which the heat is applied, and the sublimate produced is generally amorphous, or consists in part of minute granules and opaque granular masses; but it *may* contain well-defined octahedral crystals of *antimonious oxide.* The *arsenical sublimate* may be further identified by its ready solubility in a few drops of hot water, and by the resulting solution, when acidulated with hydrochloric acid and treated with sulphuretted hydrogen gas, yielding a yellow precipitate. These characters, however, reveal themselves only in sublimates obtained from comparatively thick crusts of the metal.

b. The deposits of the two metals may also be distinguished by either a solution of ammonium sulphide, or of sodium hypochlorite, or by dissolving the crust in nitric acid, evaporating the solution to dryness, and treating the residue with silver nitrate, in the manner already described for the discrimination of stains obtained on porcelain from the ignited gas.

c. If a slow stream of perfectly dry sulphuretted hydrogen gas be conducted through the tube containing the *arsenical* deposit, and the latter heated by a flame applied to the tube, beginning at the outer margin of the deposit, it in vaporizing is converted into arsenious sulphide, which condenses at a little distance in advance of the heat to a yellow deposit, the inner margin of which, even after cooling, has sometimes an orange hue. The metallic deposit from the 1–5000th of a grain of arsenious oxide will in this manner yield very distinct results. Under these same conditions, the *antimonial* crust also decomposes the sulphuretted gas, with the formation of antimonious sulphide, which, however, condenses to a reddish-brown or nearly black deposit. To effect this change requires a stronger heat than for the arsenical crust, and the sulphide formed deposits

much nearer the flame of the lamp. In applying this method, it must be borne in mind that sulphuretted hydrogen alone, especially if moist, may be decomposed by the heat with the deposition of globules of sulphur, which while warm have a yellow color, but when cold they have only a very faint yellow tint. Arsenious sulphide is readily distinguished from free sulphur in being soluble in ammonia. When exposed to a slow current of dry hydrochloric acid gas, antimonious sulphide readily disappears, whilst the sulphide of arsenic is unaffected by this gas. These methods of distinguishing between these deposits were first pointed out by Pettenkofer and Fresenius.

There is no other metal, besides arsenic and antimony, that will, by this method of Marsh, yield a deposit in the heated reduction-tube. Sulphur may yield a yellowish-white, and selenium a reddish-brown, stain; but these stains could not be confounded with the arsenical deposit.

γ. Decomposition by silver nitrate.—If the reduction-tube of the apparatus be substituted by a tube bent at a right angle (Fig. 10, *e*), and the arsenuretted hydrogen conducted into a solution of silver nitrate, both the gas and the silver salt undergo decomposition, with the production of arsenious acid, which remains in solution, and the elimination of metallic silver, which falls as a black precipitate. The reaction in this case is $AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$. The resulting solution, therefore, contains arsenious acid and free nitric acid, together with any excess of silver nitrate employed. In applying this test, which was first proposed by Lassaigne, the current of gas should not be rapid, and only a quite dilute solution of the silver salt should at first be employed; more of the salt may afterward be added, if required.

The presence of the arsenious acid thus produced may be shown by either of the following methods:

1. If the solution be filtered, and the filtrate exactly neutralized with ammonia, it will yield a yellow precipitate of silver arsenite, having the properties already described. Should the whole of the silver nitrate have been decomposed by the arsenuretted hydrogen, it will of course be necessary to add a little of this salt, after the neutralization by ammonia, before the precipitate will appear. Since in the application of this test the neutralization of the eliminated nitric acid will give rise to ammonium nitrate, in which the silver arsenite

is sparingly soluble, the reaction will not be quite as delicate as when the test is applied to a pure solution of arsenious acid.

2. If the excess of silver nitrate in the filtered solution be precipitated by slight excess of hydrochloric acid, the solution again filtered, and the filtrate treated with sulphuretted hydrogen gas, it yields a bright yellow precipitate of arsenious sulphide. The arsenic from the 1–1000th of a grain of arsenious oxide can in this manner be recovered without any appreciable loss. Instead of treating the solution with sulphuretted hydrogen, after the removal of the excess of silver nitrate by hydrochloric acid, it may be examined by Reinsch's test.

3. If, after the removal of the excess of silver nitrate by the cautious addition of hydrochloric acid, the filtrate be cautiously evaporated to dryness, the arsenic will remain as a white deposit of *arsenic acid*, which, when moistened with a solution of silver nitrate, assumes a brick-red color.

Delicacy of this reaction.—In the following investigations the arsenious oxide was dissolved in ten grains of pure water, the solution placed in a small test-tube with a few fragments of zinc, and then sufficient diluted sulphuric acid added to evolve a slow stream of gas. The gas thus evolved was conducted into five grains of a dilute solution of silver nitrate.

1. $\frac{1}{100}$ grain of arsenious oxide yields a gas that produces a copious black precipitate in the silver-solution.
2. $\frac{1}{1000}$ grain yields a good precipitate.
3. $\frac{1}{10,000}$ grain: a black deposit soon appears in the immersed end of the delivery-tube, and in a little time black flakes appear on the surface of the silver-solution.
4. $\frac{1}{100,000}$ grain: after some minutes a distinct deposit forms in the lower end of the delivery-tube.

The delicacy of this reaction depends partly upon the fact that the arsenuretted hydrogen evolved from one part of arsenious oxide eliminates six and a half parts of metallic silver.

Fallacies.—A solution of silver nitrate is also decomposed by antimonuretted hydrogen, with the production of a black precipitate. In this reaction, however, as already pointed out (*ante*, 230), the whole of the antimony, even to the last trace, is thrown down as silver antimonide. This method will, therefore, serve to separate and detect arsenic in the presence of antimony, even, according to Dr.

Hofmann, when the mixture consists of one part of the former and one hundred and ninety-nine parts of the latter metal, and only a minute quantity of the mixture is examined.

So, also, will sulphuretted hydrogen and the hydride of phosphorus produce black precipitates in a solution of silver nitrate. It is obvious, therefore, that the mere production of a black precipitate, in the silver-solution, is not in itself direct evidence of the presence of arsenic.

When arsenuretted hydrogen is passed into a solution of *corrosive sublimate* it produces a yellow or brownish-yellow precipitate, which, according to H. Rose, consists of $As_2 3Hg_2Cl_2$,—the reaction being, perhaps, $2AsH_3 + 6HgCl_2 = 6HCl + As_2 3Hg_2Cl_2$. Antimonuretted hydrogen, under like circumstances, produces a white, flocculent precipitate, which almost immediately turns gray, then dark gray or almost black. The reaction of the arsenuretted gas is extremely delicate. Thus, the gas evolved from the 1–50,000th of a grain of arsenious oxide in ten grains of fluid will produce a quite distinct yellow deposit in the lower end of the delivery-tube.

Since arsenuretted hydrogen is thus decomposed by salts of silver and of mercury, as well as by free chlorine, nitric acid, and certain other substances, if either of these be present in the flask in which the gas is being generated, the latter may be entirely decomposed before leaving the apparatus. It is, therefore, obvious that if in the examination of a suspected mixture by the method of Marsh it should yield negative results, it would not follow, from this fact alone, that arsenic was entirely absent, even in a soluble form.

M. Z. Roussin has recommended, for the evolution of the hydrogen in the application of Marsh's test, to substitute for the zinc metallic *magnesium*, which may now be obtained in its pure state. If this metal be employed, before introducing the arsenical or suspected solution into the apparatus the evolved gas should be examined by passing it through the red-hot reduction-tube for about ten minutes, for the purpose of testing its purity. This preliminary examination is necessary, since magnesium is sometimes contaminated with silicium, which might give rise to silicuretted hydrogen, with the deposition of a dark brown deposit in the heated tube. This deposit, however, differs from an arsenical crust in that it is un-

affected by nitric acid and by a solution of a hypochlorite, it being insoluble in these liquids. (*Chem. News*, July, 1866, 27, 42.)

BLOXAM'S METHOD.—When arsenious acid is present in a mixture in which water is being decomposed by a galvanic current instead of by zinc and sulphuric acid, the arsenical compound is also decomposed by the nascent hydrogen with the formation of arsenuretted hydrogen gas. Prof. Bloxam has proposed this reaction as a ready means of detecting arsenic, and as free from some of the objections that may be urged against the method of Marsh.

The form of apparatus he employs consists of a two-ounce narrow-mouthed bottle, the bottom of which has been cut off and replaced by a piece of vegetable parchment tightly stretched over it and secured by a thin platinum wire. The bottle is furnished with a cork, carrying a funnel-tube, and a small tube bent at a right angle and connected with the reduction-tube by a caoutchouc connection; through the cork also passes a platinum wire bent into a hook, inside of the bottle, for suspending the negative plate. The bottle is placed in a glass vessel of such size as to leave a small interval between the two, and this arrangement placed in a large vessel of cold water; an ounce of diluted sulphuric acid is then introduced into the apparatus, so as to fill the bottle and the outer space to about the same level, the positive plate being immersed in the acid contained in this outer space.

The apparatus being thus adjusted, the terminal platinum plates, each measuring about two inches by three-quarters of an inch, are connected by means of broad strips of platinum-foil with a Grove's battery of five cells; the one within the bottle being connected with the zinc, and that in the outer vessel with the platinum extremity of the battery. When the bottle has become filled with hydrogen, the reduction-tube—which may be constricted at several places—is heated to redness for about fifteen minutes, to test the purity of the sulphuric acid employed. The liquid to be tested is then introduced into the bottle by means of the funnel-tube, and the gas evolved examined in the same manner as in Marsh's method. If the mixture froths, from the presence of organic matter, a little alcohol may be added. The author of this method states that by it the 1–1000th of a grain of arsenious oxide can be detected in an organic mixture with the greatest ease and certainty.

When the metal exists in the form of *arsenic acid*, no arseniuretted hydrogen is evolved by this process. When in this form, however, the arsenic may be made to respond to the test by treating the solution, previous to its introduction into the apparatus, with sulphurous acid gas or a few drops of a solution of sodium disulphite, and heating on a water-bath until the sulphurous odor has disappeared. The introduction of a few drops of a solution of sulphuretted hydrogen gas into the apparatus also serves to reduce the arsenic acid, as the arsenic combines with the nascent hydrogen in preference to the sulphur; even when large excess of sulphuretted hydrogen is employed, it does not interfere with the evolution of the arseniuretted gas. But under these circumstances a deposit of sulphur may form in the reduction-tube outside of the arsenical deposit, and the latter may consist partly of arsenious sulphide; the sulphide of arsenic may be distinguished from free sulphur by its deep yellow color, and its ready solubility in a warm solution of ammonium carbonate, in which the sulphur is insoluble.

The addition of sulphuretted hydrogen to the arsenical solution, under the above circumstances, would precipitate as a sulphide any antimony or mercury if present, in which form neither of these metals interferes with the detection of arsenic. Thus, Prof. Bloxam states that the 1–1000th of a grain of arsenious oxide, converted into arsenic acid, by the action of hydrochloric acid and potassium chlorate, when mixed with one grain of tartar emetic and excess of sulphuretted hydrogen, and the mixture introduced into the decomposing cell, furnished in the reduction-tube a distinct deposit of arsenic free from antimony. Similar experiments made with mixtures of arsenious acid and corrosive sublimate furnished equally good results. Without the addition of the sulphuretted hydrogen, the antimony and mercury are deposited upon the negative plate; when, however, a comparatively large quantity of the former metal was present, it yielded a metallic mirror in the reduction-tube. (*Quart. Jour. Chem. Society*, xiii. 12, 338.)

Various other modifications of Marsh's method have been proposed. Thus, Fleitmann has advised to generate the hydrogen by acting upon zinc with a warmed solution of potassium hydrate, instead of diluted sulphuric acid. Any arsenic now added, if in solution, would be evolved as arseniuretted hydrogen, while if antimony

were present it would be retained in the metallic state by the alkaline solution. Zinc, however, acts only very slowly upon the alkaline solution, and even if iron filings be added, as has been advised to hasten the action, we do not find the method advisable.

Dr. E. W. Davy has proposed to employ an amalgam of sodium for generating the hydrogen, and thus do away with the use of an acid and employ two metals which are not liable to arsenical contamination. The amalgam proposed consists of one part by weight of sodium to eight or ten parts of mercury, and is prepared by moderately heating the mercury in a test-tube and then adding the sodium, small portions at a time. The metals readily unite to form an alloy. The contents of the tube, while still hot and liquid, are poured out on a clean plate, and when cold broken into small lumps, which are preserved in a well-stoppered bottle.

To employ the amalgam, the suspected solution is placed in a test-tube, a small portion of the amalgam added, and the mouth of the tube quickly covered with a piece of filtering-paper moistened with a solution of silver nitrate. Any arsenic present will now give rise to arsenuretted hydrogen and cause the moistened paper to acquire a dark brown or dull black color, due to the reduction of the silver salt by the evolved arsenical gas. (*Chem. News*, Feb. 1876, 58.) The delicacy of the reaction of arsenuretted hydrogen with silver nitrate solution has already been pointed out. The mere reduction or blackening of the silver salt, however, should not be accepted as positive proof of the presence of arsenic.

Otis Johnson has proposed to evolve the hydrogen by the action of metallic aluminium upon a warmed saturated solution of potassium hydrate. (*Chem. News*, Dec. 1878, 301.)

6. *Bettendorff's Test.*

When a solution of arsenious oxide or of arsenic oxide is added to a strong hydrochloric acid solution of stannous chloride, the arsenical compound is reduced with the separation of metallic arsenic. To apply this test, a small quantity of the tin chloride is dissolved in about half a drachm or two cubic centimetres of strong hydrochloric acid contained in a test-tube, a drop or two of the arsenical solution added, and, if necessary, the mixture gently warmed, when it will assume a brownish color, and after a time yield a brownish or grayish-brown precipitate consisting chiefly of metallic arsenic,

the liquid becoming colorless. The delicacy of the reaction is somewhat increased by adding to the mixture about half its volume of concentrated sulphuric acid.

Under the action of the test, 1–100th of a grain of arsenious oxide will yield an immediate brown coloration, and after a time a very decided precipitate. 1–10,000th of a grain, when forming only 1–500,000th of the hydrochloric acid mixture, will yield a marked brown coloration, and after a time a perceptible brownish deposit. This is about the limit of the reaction.

Other Reactions of Arsenious Acid.—Various other tests have been proposed for the detection of arsenious acid, but in regard to both delicacy of reaction and freedom from fallacy they are much inferior to those already described. Among these tests may be mentioned the following.

1. *Lime-water* produces in solutions of the oxide a white precipitate of calcium arsenite, which is readily soluble in hydrochloric and most other acids. One grain of a 1–100th solution of arsenious oxide yields a copious, flocculent precipitate, which soon becomes granular; a similar quantity of a 1–1000th solution yields a very good granular deposit; and the same quantity of a 1–5000th solution, a slight cloudiness. The whole of the arsenic may be withdrawn from the hydrochloric acid solution of the arsenite by Reinsch's test. The lime reagent also produces white precipitates in solutions of several other acids.

2. *Potassium iodide* slowly throws down from concentrated solutions of arsenious acid a white, granular precipitate, which adheres tenaciously to the sides and bottom of the test-tube in which the experiment is performed. The deposit, when treated with hydrochloric acid, assumes a bright yellow color. Ten grains of a 1–50th solution of the oxide fail to yield with the reagent a precipitate for several minutes; after about an hour a copious deposit has formed. If, after the addition of the reagent, the mixture be treated with large excess of hydrochloric acid, it yields an immediate orange-yellow or yellow precipitate, which is insoluble in hydrochloric acid, but readily soluble in excess of arsenious acid. In this manner the 1–100th of a grain of the oxide in one grain of water yields a copious, orange-yellow deposit; and the 1–1000th of a grain, a quite good yellow precipitate. If the arsenious acid be added to a solution

of potassium iodide in large excess of hydrochloric acid, the same yellow precipitate separates.

3. When a solution of arsenious acid is treated with excess of caustic potash and a drop of a solution of copper sulphate, the mixture on being boiled throws down a red precipitate of copper suboxide, due to the reducing action of the arsenious acid, the latter remaining in solution as arsenic acid. In the addition of the copper solution, care should be taken to avoid an excess, otherwise the mixture will also yield a black precipitate of copper monoxide, which may mask the color of the suboxide. Solutions of grape-sugar and of certain other substances have a reducing action similar to that of arsenious acid.

Separation from Organic Mixtures.

Suspected Solutions.—Since arsenious oxide, under certain conditions, is only sparingly soluble in water, before applying any chemical tests to a suspected mixture containing solid organic matter it should be carefully examined for solid particles of the poison. If the mixture contain much mechanically suspended matter, the whole may be placed in a large porcelain dish, water added if necessary, and the mass thoroughly mixed; the larger organic masses are then carefully removed, the remaining contents gently rotated in the dish, the supernatant liquid decanted, and the residue carefully examined, by means of a lens if necessary, for the solid oxide. Any white masses or particles thus found are washed in pure water and allowed to dry. A very small portion of the dried mass is then heated in a small reduction-tube, and any sublimate obtained examined by the microscope. Other portions of the mass may be examined by any of the other tests already described for the recognition of the oxide in its solid state. So, also, a portion may be dissolved in water and the solution tested.

Whether the poison is thus discovered or not, the organic solids are returned to the liquid and the whole intimately mixed, the liquid then filtered, and the solids on the filter washed with distilled water, the washings being added to the first filtrate. Should the mixture presented for examination be thick from the presence of organic matter, after the addition of water and before filtration, it may be acidulated with hydrochloric acid and gently boiled for ten or fifteen minutes. The filtrate, obtained by either of these methods, is con-

centrated to a convenient volume, measured, and a given portion set aside for a quantitative analysis if necessary. Another portion, acidulated with hydrochloric acid, is boiled with a very small slip of bright copper-foil, the latter not being added until the liquid has reached the boiling temperature. If the copper quickly receive a coating, it is removed from the liquid, and fresh slips of the metal added, as long as they receive a deposit. Should, however, the copper first added not receive a metallic coating, the boiling should be continued until the liquid is evaporated to near dryness before it is concluded that the poison is entirely absent. Any slips of copper that have thus become coated are washed by the aid of a gentle heat, first in pure water, then in water containing a trace of ammonia, and again in pure water, then drained, placed on filtering-paper, and dried in a water-bath. One or more of the coated slips are then heated in an appropriate reduction-tube, when the deposit, if consisting of arsenic, will yield a sublimate of octahedral crystals of arsenious oxide, readily identified by means of the microscope.

If the method now considered should fail to reveal the presence of arsenic, there would be little doubt of the entire absence of the poison, unless, possibly, there was also some other substance present that interfered with its deposition upon the copper; at the same time, if the copper remained bright, it would be quite certain that mercury and antimony also were absent.

Should it be desired to pursue the investigation, another portion of the above filtrate may be examined after the method of Marsh. Or, the liquid, acidulated with hydrochloric acid, may be saturated with sulphuretted hydrogen gas, and allowed to stand in a moderately warm place until the precipitate has completely subsided; the precipitate is then collected on a filter, washed, and, if it contains organic matter, purified in the manner hereafter described.

Vomited matters.—These are carefully collected, and examined for any solid particles of the poison. The mass is then diluted with water, strongly acidulated with hydrochloric acid, and kept at about the boiling temperature for about twenty minutes; after the mixture has cooled, the liquid is filtered, the filtrate concentrated, and then examined in the manner directed above. It need hardly be remarked that a failure to detect the poison in the vomited matters would not in itself be conclusive evidence that it had not been taken.

Contents of the Stomach.—Before proceeding to the preparation of the contents of the stomach for the application of chemical tests, they, as well as the inside of the organ, should be minutely examined for any of the poison in its solid state, in the manner described above. Any white particles or powder thus found are washed, dried, and tested in the usual manner for the solid poison. The physical appearance and condition of the stomach should also be carefully noted.

The contents are now placed in a clean porcelain dish, and the inside of the stomach scraped and washed, the scrapings and washings being added to the contents of the dish; or the tissue itself may be cut into small pieces, and these added to the contents. After the addition of water if necessary, the mass is intimately mixed with about one-eighth of its volume of pure hydrochloric acid, and maintained at near the boiling temperature until the organic solids are entirely disintegrated. The mixture is then allowed to cool, transferred to a clean muslin strainer, and the matters retained by the strainer washed with water: the strainer, with its contents, may be reserved for future examination, if necessary. The strained liquid thus obtained, if in large quantity, is concentrated at a moderate heat, again allowed to cool, and then filtered.

A given portion of the filtrate thus obtained is examined by the method of Reinsch, successive slips of the copper being added as long as they receive a deposit. Any pieces of the metal that have thus become coated, after being thoroughly washed and dried, are heated in a suitable reduction-tube, and the result examined in the usual manner.

Another portion, or the whole of the remaining filtrate, may be exposed for several hours to a slow stream of washed sulphuretted hydrogen gas, then gently warmed, and allowed to stand quietly until the supernatant liquid has become perfectly clear. If the poison is present in considerable quantity, the precipitate may have a bright yellow color and consist of nearly pure arsenious sulphide; the color of the latter, however, may be much modified by the presence of organic matter, which is always more or less precipitated under these circumstances, usually of a yellowish-brown color.

The precipitate thus produced is collected upon a small filter, washed, and, while still moist, digested with pure aqua ammoniæ: this liquid will readily dissolve any arsenious sulphide present, while

the organic matter may remain undissolved. The ammoniacal solution is filtered, and the filtrate carefully evaporated at a moderate heat to dryness. The true nature of the residue thus obtained, if consisting of arsenious sulphide, may be established by either of the methods heretofore pointed out, under the special consideration of the sulphuretted hydrogen test. Should, however, the residue contain organic matter and only a minute quantity of the sulphide, it may require further purification before its arsenical nature can be satisfactorily determined. Under these circumstances, the dried residue is collected in a thin porcelain dish or crucible, moistened with a few drops of concentrated nitric acid, and treated in the manner described hereafter, for the purification of the sulphuretted hydrogen precipitate obtained from the tissues.

The *contents of the intestines* may be examined in the same manner as the contents of the stomach. Sometimes the poison may be detected in these when there has been a failure to show its presence in the stomach.

From the Tissues.—Whether the examination of the contents of the stomach or of the intestines have revealed the presence of arsenic or not, an examination of the tissues or fluids of the body, for the absorbed poison, should not be omitted. Any poison found under these circumstances would be that which had entered the circulation and had its share in producing death; whereas this would not be the case with that found in the contents of the stomach or intestines. Moreover, it sometimes happens that the poison is absent from the alimentary canal, and yet readily detected in some of the tissues. Absorbed arsenic is deposited, to a greater or less extent, in all the soft tissues of the body, and any of these may be made the subject of analysis; the greatest relative quantity, however, is usually found in the liver. The absolute quantity thus found, even under the most favorable circumstances, rarely exceeds a grain in weight.

For the recovery of *absorbed* arsenic from the tissues various methods have been proposed. In many instances this may be effected by simply boiling the finely divided tissue with diluted hydrochloric acid until the organic matter is well disintegrated, and then employing the method of Reinsch. In this manner we have, in several instances, recovered sufficient of the poison from the liver to permit its confirmation by all the other tests. The more certain method of proceeding, however, is to destroy entirely, or at least

carbonize, the organic matter before applying any tests. For this purpose the following methods have been advised.

1. *Fresenius* and *Babo* proposed to destroy or disintegrate the organic matter by means of hydrochloric acid and potassium chlorate, under the action of heat. For this purpose we have found the following proportions of tissue, acid, and the chlorate yield very satisfactory results. Three hundred grammes, or ten ounces, of the solid tissue, as of the liver, cut into very small pieces and placed in a clean porcelain dish, are treated with a mixture of sixty cubic centimetres, or two fluid-ounces, of strong hydrochloric acid and two hundred and forty cubic centimetres, or eight fluid-ounces, of water. The mixture is heated on a sand-bath, and when at about the boiling temperature, about one gramme, or fifteen grains, of powdered potassium chlorate added, and the addition repeated, with frequent stirring, every several minutes, until about six or seven grammes, or one hundred grains, have been added and the mass has become homogeneous and of a light yellow color. During this process a little water should occasionally be added, to prevent concentration of the liquid. The disintegrating action of this mixture is chiefly due to the free chlorine and chlorine peroxide evolved by the mutual decomposition of the chlorate and a portion of the hydrochloric acid; thus: $4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + Cl_9$. The disintegrated mass is moderately heated until the odor of chlorine has entirely disappeared, and is then allowed to cool.

The cooled mixture is transferred to a linen strainer, and, when the liquid has all passed, the solids are washed with a little warm water, the washings being collected separately. These are concentrated on a water-bath to a small volume, allowed to cool, then added to the first strained liquid, and the mixed liquid filtered through paper. Any arsenic present will now exist as arsenic acid.

The filtrate thus obtained is exposed to a slow stream of *sulphurous anhydride*, known also as sulphurous acid gas,—prepared by boiling slips of copper with concentrated sulphuric acid,—or treated with a solution of acid sulphite of sodium (bisulphite) until it smells strongly of the gas. Uuder this treatment any arsenic acid present will be reduced to arsenious acid, in which form the metal is not only much more rapidly, but also, as we have found by experiment, more completely precipitated by sulphuretted hydrogen than when it exists in the form of arsenic acid. The reducing action of the

gas is as follows: $H_3AsO_4 + SO_2 + H_2O = H_2SO_4 + H_3AsO_3$. The liquid is now concentrated on a water-bath at a moderate heat to a volume twice that of the hydrochloric acid employed in preparing the mixture. We have found that the liquid may be concentrated quite to this extent without any loss of arsenic, even when the metal is present in only very minute quantity. The concentrated liquid is allowed to stand in a cool place for several hours, and then filtered.

The filtrate thus obtained is exposed to a slow stream of washed sulphuretted hydrogen gas transmitted through the liquid for several hours; it is then gently warmed, and allowed to stand in a moderately warm place for from twelve to twenty-four hours. Any arsenic present will thus be precipitated as arsenious sulphide, together with more or less organic matter and free sulphur. Should the liquid contain mercury, antimony, copper, or lead, these metals would also be precipitated, as sulphides, by the sulphuretted hydrogen. It must be borne in mind that liquids prepared as the above usually yield with sulphuretted hydrogen a brownish or yellowish precipitate of organic matter and free sulphur, even in the absence of any metal. The precipitate is now collected upon a small filter, and washed, at first with water containing a little sulphuretted hydrogen, until the washings no longer contain chlorine.

For the *purification of the precipitate* thus obtained different methods have been proposed. The following method, advised by Prof. Otto, has in our hands furnished very satisfactory results. The filter containing the moist precipitate is spread out in a porcelain dish, and the precipitate thoroughly stirred with a diluted solution of ammonia (1 in 10), which will readily dissolve any arsenious sulphide present, with more or less of the organic matter and free sulphur: one part of the sulphide, when moist, is readily taken up by forty parts of the diluted ammonia. The sulphides of the other poisonous metals mentioned above, which might be present, would remain unchanged under the action of the ammoniacal liquid, except perhaps a mere trace of the antimony sulphide. The ammoniacal mixture is transferred to a small, moistened filter, and the solid residue washed with diluted ammonia, the washings being collected with the first filtrate. The filter, with its contents, should be reserved for future examination, if necessary.

The ammoniacal filtrate, which has usually a dark brown color, is now placed in a small porcelain capsule or thin evaporating-dish,

and evaporated to dryness on a water-bath; the residue is treated with a small quantity of concentrated nitric acid, and the mixture again evaporated to dryness, this operation with nitric acid being repeated, if necessary, until the moist residue has a yellow color. The residue is then moistened with a few drops of a concentrated solution of caustic soda, a small quantity of pure powdered sodium carbonate and sodium nitrate added, and the well-mixed mass cautiously evaporated to dryness; the heat is then very gradually increased until the fused mass becomes colorless, when the organic matter will be entirely destroyed. In the performance of the operations now described it is of the utmost importance that the nitric acid and the sodium compounds employed be perfectly free from chlorine, since otherwise a portion or the whole of the arsenic may be volatilized in the form of chloride.

Any arsenic present will now exist, in the incinerated residue, as sodium arsenate, mixed with more or less nitrate, nitrite, carbonate, and sulphate of sodium, the latter salt being derived from the oxidation of the sulphur. This mixture, when cooled, is dissolved in a small quantity of warm water, and the solution, after filtration if necessary, strongly acidulated with pure sulphuric acid, then evaporated until fumes of sulphuric acid are evolved. By this treatment the carbonic, nitric, and nitrous acids will be entirely expelled, the sodium combined with them uniting with the sulphuric acid to form sodium sulphate: the solution will, therefore, contain only sodium sulphate, and sodium arsenate, if present. Should there be any doubt as to the entire expulsion of the nitric and nitrous acids, a little more sulphuric acid is added, and the solution again evaporated.

Instead of destroying the organic matter by fusion with sodium carbonate and nitrate in the manner above described, the nitric acid residue mentioned above, after addition of a drop of caustic alkali, may be treated with a few drops of concentrated sulphuric acid, and the mass heated on a sand-bath until it becomes about dry; the residue is again moistened with the concentrated acid, and heated in the same manner until fumes of the acid are no longer evolved. The carbonaceous residue, pulverized if necessary, is then boiled with a small quantity of water containing a drop or two of sulphuric acid; the cooled liquid is filtered, and the carbonaceous matter washed with warm water until all soluble matter is removed. If in the carbonization the whole of the free sulphuric acid was expelled, the

resulting solution will be colorless and entirely free from organic matter. The liquid may now be concentrated to a small and given volume. This method is somewhat more simple and expeditious than that described above, and yields about equally good results.

A portion of the final solution obtained by either of the foregoing methods may now be introduced into an active Marsh's apparatus, and the evolved gas examined in the manner already described. Before submitting any remaining portion of the suspected liquid to the action of any of the other tests, the arsenic acid should be reduced to arsenious acid, by sulphurous acid gas, in the manner heretofore directed. A portion of the solution may now be examined by the method of Reinsch, and another portion submitted to the action of sulphuretted hydrogen gas. Any arsenious sulphide precipitated from a solution of this kind, especially if only a small quantity of the metal be present, will usually have a more or less brownish or orange hue. The arsenical nature of any arsenious sulphide thus obtained may be confirmed by any of the methods heretofore described, especially by the process of reduction. If the first examination of the suspected liquid by Marsh's method indicate the presence of a comparatively large quantity of arsenic, a given portion of the solution should be employed for the application of the sulphuretted hydrogen test, and the quantity of the sulphide thus obtained estimated in the manner hereafter described. If any of the suspected solution, that has been treated with sulphurous acid gas, still remain, and it be desired to apply the silver and copper tests, a small quantity of the liquid is *exactly* neutralized by caustic soda or sodium carbonate, then divided into two about equal parts, to one of which a solution of silver nitrate and to the other a solution of copper sulphate is added, when any arsenic present will yield its appropriate precipitates. Since, under the circumstances just mentioned, the arsenic would exist in the neutralized liquid as an alkali arsenite, the ammonio-compounds of the silver and copper salts should not be employed.

The method now described for the disintegration of the tissues, and the subsequent purification of the precipitate produced by sulphuretted hydrogen, is, according to our experience, the best yet proposed for the recovery, at least of minute traces, of absorbed arsenic. At the same time, it has the advantage of excluding mercury, antimony, and certain other poisonous metals from the solution tested

for arsenic, and yet provides for their detection if present in the substance submitted to examination. In illustration of the delicacy of this process, in regard to the purification of the sulphuretted hydrogen precipitate, the following experiment may be cited. A partially decomposed liver, free from arsenic, was boiled with diluted hydrochloric acid and potassium chlorate until the organic matter was well disintegrated, and to one thousand fluid-grains of the complex mixture thus obtained the 1–100th of a grain of arsenious oxide, in solution, was added,—the oxide forming only the 1–100,000th of the mixture. The mixture was then gently heated, allowed to cool, and the strained liquid treated with a slow stream of sulphuretted hydrogen for twenty-four hours; the precipitate thus obtained—which purposely contained an excess of organic matter—was then treated as described above, by fusion with sodium carbonate and nitrate, when the final solution, after treatment with sulphurous acid gas, gave with several reagents results that could scarcely be distinguished from those obtained from an equal volume of pure water containing the 1–100th of a grain of the poison.

In a second experiment, the 1–100th of a grain of arsenious oxide was added to the tissue of a stomach and its contents free from arsenic, the added arsenic forming only 1–600,000th of the mixture, and the whole treated in the foregoing manner without any marked loss of the arsenic.

In a third experiment, the 1–100th of a grain of arsenious oxide, when forming only the 1–600,000th part of a liver-mixture, treated after the above method furnished a final solution, the 1–10th part of which in each case, when examined respectively by Marsh's, Reinsch's, and the sulphuretted hydrogen methods, yielded perfectly satisfactory evidence of the presence of arsenic.

For the purification of the sulphuretted hydrogen precipitate produced from organic mixtures, Fresenius recommends to moisten it, together with the filter, with fuming nitric acid, evaporate to dryness on a water-bath, moisten the residue with warmed concentrated sulphuric acid, then heat it for two or three hours on a water-bath, and finally on an oil-bath to a temperature of about 170° C. (338° F.), until the charred mass becomes friable, and a sample of it no longer imparts a color when mixed with water. The mass is then warmed with a mixture of eight parts of water and one part of hydrochloric acid, the solution filtered, the filtrate precipitated by

sulphuretted hydrogen, the precipitate collected on a small filter, washed, redissolved in ammonia, the ammoniacal solution evaporated to dryness, and the residue weighed. The residue may then be reduced by a mixture of potassium cyanide and sodium carbonate, in an atmosphere of carbon dioxide, in the manner already described.

In this connection it may be remarked that the soft animal tissues may be broken up and dissolved by heating them, after being cut into small pieces, with diluted hydrochloric acid alone, without the subsequent addition of potassium chlorate. But under these circumstances they require prolonged heating, and the resulting solution, when strained, is apt to be viscid and have a very dark or nearly black color, both of which are objectionable if the liquid is to be subsequently treated with sulphuretted hydrogen. A more serious objection, however, is that if arsenic be present in the form of sulphide, which is not unfrequently the case when the parts have undergone putrefaction, the whole of it may escape solution. To a liquid prepared in this manner the method of Reinsch may, of course, be directly applied; whereas this will not be the case when the solution has been prepared by means of potassium chlorate.

That the method of Reinsch will serve to recover very minute quantities of arsenic from complex solutions is well illustrated by the following experiment. The 1–1000th of a grain of arsenious oxide, in solution, was added to one hundred fluid-grains of the complex mixture obtained by boiling a stomach with its contents, free from arsenic, with diluted hydrochloric acid. The mixture was then boiled with a small slip of bright copper-foil, when after a little time the foil received a very good steel-like coating, which, when heated in a small contracted reduction-tube, furnished a fine octahedral crystalline sublimate, very similar to that obtained in a like manner from the 1–100th of a grain of the oxide in solution in one hundred grains of pure acidulated water. It will be observed that in this case the poison was diffused in 100,000 times its weight of the organic liquid.

2. For the recovery of absorbed arsenic from the tissues M. A. Gautier has recently advised the following method. (*Ann. d'Hyg.*, Jan. 1876, 138.) 100 grammes of the solid tissue, finely divided and placed in a porcelain dish of about 600 cubic centimetres capacity, are treated with 30 grammes of pure nitric acid, and moderately heated. The mass slowly liquefies and assumes an orange hue. The dish is then removed from the heat, and 5 grammes of pure sulphuric

acid added. The mass now becomes brown and is violently attacked. It is then heated till vapors of sulphuric acid appear. The residue is treated with 10 or 12 grammes of nitric acid, added small portions at a time; this causes the mass to again liquefy, and it evolves dense nitrous vapors. When all the acid has been added, the mass is heated until it begins to carbonize. The easily pulverized residue thus obtained is exhausted by boiling water. The filtered liquid, of a more or less clear wine color, is treated with a little sodium sulphite, and the arsenic precipitated as sulphide by a prolonged current of sulphuretted hydrogen gas. The sulphide is transformed into arsenic acid in the ordinary manner, and introduced into a Marsh's apparatus.

In experiments after this method, in which small quantities of arsenious oxide were added to animal tissues, and the blood, M. Gautier recovered very nearly the total theoretical quantity of the metal. And in our own experiments the method has given very excellent results. On applying this method, however, to the examination of 300 grammes of the liver of a large dog killed by arsenic, 0.32 milligramme (1–200th grain) of metallic arsenic was obtained; whereas an equal quantity of the same organ when disintegrated by hydrochloric acid and potassium chlorate, and the solution treated as before, furnished 0.52 milligramme (1–125th grain) of the metal. It may be, however, that in this instance the arsenic was not equally distributed throughout the liver.

3. Danger and Flandin proposed to destroy the organic matter of the tissues by means of concentrated sulphuric acid. The tissue, cut into small pieces, is treated with about one-fourth its weight of the concentrated acid, and the mixture heated in a porcelain dish until the black pasty mass first produced becomes dry and carbonaceous; the cooled mass is then treated with a little concentrated nitric acid, or aqua regia, and again evaporated to dryness. The mass is now treated with boiling water, the solution acidulated with nitric acid, then evaporated to dryness, the residue moistened with nitric acid, and the liquid again expelled by a moderate heat, this operation with nitric acid being repeated, if necessary, until the mass becomes colorless. The mass is then dissolved in a little water, the solution neutralized with sodium carbonate, evaporated to dryness, and the residue again heated with a few drops of concentrated sulphuric acid. Any arsenic present will now exist as sodium arsenate. The residue is then dissolved in a small quantity of warm water, and the solution

examined by the method of Marsh; or, the solution may be saturated with sulphurous acid gas, and, after gently heating the liquid to expel the excess of gas, treated with sulphuretted hydrogen.

The objection to the method of Danger and Flandin is that if a chloride, as sodium chloride, or common salt be present, the carbonization with sulphuric acid may give rise to the volatilization, in the form of trichloride, of any arsenic present. The same objection would hold against the employment of aqua regia in the process. To meet these objections, it has been proposed to conduct the operations in a retort connected with a well-cooled receiver.

4. Duflos and Hirsch, in 1842, advised to treat the finely divided tissue, placed in a retort, with about an equal weight of pure concentrated hydrochloric acid. A cooled receiver, containing a little water, is then connected with the retort, and the latter heated on a chloride of calcium bath until the contents become of a pasty consistency. This residue is mixed with about twice its weight of strong alcohol, the mixture allowed to digest some time, the liquid then strained through muslin, and the solid matter well washed with fresh alcohol. The mixed alcoholic liquids are filtered, and the filtrate distilled in a retort until the alcohol passes off, after which the residue is mixed with the acid contents of the receiver of the first distillation. This mixture, after cooling, is treated with sulphuretted hydrogen, when any arsenic present will be precipitated as sulphide.

Since arsenious acid, when heated with concentrated hydrochloric acid, is converted into arsenious chloride, which is volatile, it has recently been proposed to take advantage of this fact for the complete separation of the poison from the tissues, as well as from organic mixtures generally. The finely divided tissue, or the residue obtained by evaporating the suspected organic solution to dryness, is thoroughly dried on a water-bath, then placed in a retort with about its own weight of concentrated hydrochloric acid, and the mixture distilled on a sand-bath to almost dryness, the distillate being collected in a well-cooled receiver containing a little water; the residue in the retort may be redistilled with a fresh portion of the acid.

The distillate thus obtained contains the arsenic as trichloride, together with a large quantity of free hydrochloric acid, and more or less organic matter. A portion of the distillate may be examined after the method of Reinsch. The remaining liquid, diluted if necessary, is examined by the sulphuretted hydrogen test or by the

process of Marsh, or both, and the results confirmed in the ordinary manner. Since the liquid contains a large quantity of free hydrochloric acid, this may interfere with the detection of minute traces of the poison by the method of Marsh. The only metals, besides arsenic, that could, under these circumstances, appear in the distillate are antimony, bismuth, and perhaps tin. Should the arsenic exist in the substance subjected to distillation, in the form of sulphide, it would not appear in the distillate. Under these circumstances, the residue in the retort may be heated with diluted hydrochloric acid and the occasional addition of potassium chlorate, until the organic matter is destroyed; the resulting solution is then treated with sulphurous acid gas, and subsequently with sulphuretted hydrogen, in the manner heretofore described.

So, also, if the arsenic exists as arsenic acid it will not appear in the distillate as trichloride, unless first reduced to arsenious acid. For this reduction E. Fischer advises (1880) ferrous chloride, and he finds that when arsenic acid is distilled with hydrochloric acid and ferrous chloride, it is quickly reduced and completely converted into volatile trichloride, while all the other metals of the sulphuretted hydrogen group, including antimony and tin, remain behind with the iron.

5. As an easy and rapid method for the recovery of arsenic from complex mixtures, T. D. Boeke has advised (*Chem. News*, April, 1880, 177) to heat the substance with hydrochloric acid and potassium chlorate until the mass has assumed a liquid form. The liquid when cold is filtered, and the residue washed with water. The yellow filtrate is treated with sodium carbonate to strongly alkaline reaction, and evaporated until sodium chloride begins to separate. The liquid is then again treated with hydrochloric acid and potassium chlorate, filtered, and treated with excess of ammonia. Addition of the "magnesium mixture" will now precipitate any arsenic present as ammonium-magnesium arsenate, together with ammonium-magnesium phosphate. After twenty-four hours the precipitate is collected, washed with diluted ammonia till free from chlorine, then dissolved in diluted sulphuric acid, the arsenic acid reduced by sulphurous acid, and the metal precipitated by sulphuretted hydrogen as arsenious sulphide.

From the Urine.—A large quantity of the urine, as 250 c.c., or 8 fluid-ounces, concentrated to a syrup, may be treated with sufficient

nitric acid to decompose the urea, and, after the violent action has ceased, the liquid evaporated to a thick syrup. This is treated with sulphuric acid and heated on a sand-bath until the mass is nearly dry; it is again moistened with the acid and heated until the whole of the acid is expelled. The pulverized residue is boiled with water containing a drop or two of sulphuric acid, the liquid filtered, and the solids washed with water. The filtrate, after addition of sulphurous anhydride, is concentrated to something less than one-tenth the volume of the urine employed, or until saline matter begins to separate. It is then, after filtration if necessary, treated with a slow current of sulphuretted hydrogen gas, and any arsenious sulphide precipitated purified and examined in the manner already directed.

The urine seems to be the principal channel through which arsenic is eliminated from the system. In a case related by Dr. Maclagan, he detected a trace of the poison in twenty-six ounces of urine as late as the twenty-first day after it had been taken. In a case reported by Dr. Gaillard (*Ann. d'Hyg.*, Oct. 1874, 407), a young woman, for the cure of an obstinate eczema, took, under the form of Fowler's solution, one-fourth grain of arsenious oxide daily for fifteen days; then one-third grain for the same period; and finally one-half grain for some days. Marked symptoms of chronic poisoning having appeared, the medicine was discontinued. On examination of the urine, arsenic was found present, and it continued to be eliminated for *six and a half weeks* after the medicine had been discontinued. After this period the arsenical paralysis rapidly disappeared.

Distribution of Absorbed Arsenic.—It was first announced by Orfila, in 1839, that when arsenic is taken into the system it is sooner or later absorbed and distributed to the blood, tissues, and various secretions of the body. Subsequent examinations indicated that the absorbed poison was for the most part usually deposited in the liver, kidneys, and spleen.

More recently, however, M. Scolosuboff concluded, from experiments upon animals poisoned by sodium arsenite, that the absorbed poison was deposited chiefly in the brain and spinal cord; and that if the absorbed metal present in a given quantity of fresh muscle be taken as 1, that in the liver is 10.8, in the brain 36.5, and in the spinal marrow 37.3. (*Ann. d'Hyg.*, 1876, 153.) More recent examina-

tions, however, have shown this conclusion to be erroneous, and that usually a smaller proportion of the absorbed poison is present in the nerve-tissue than in certain other tissues of the body, especially the liver and kidneys.

On examining the liver, brain, one kidney, and the muscles of a man who died from the effects of arsenic, Prof. Ludwig found the relative proportions of arsenic in a given weight of the different organs to be as follows: brain, 1; muscles, 3; liver, 84; kidney, 129; that is, a given quantity of the kidney contained 129 times more of the metal than was found in an equal quantity of the brain. (*Ann. d'Hyg.*, Jan. 1882, 88.) In a still more recent case, J. Guareschi found in the viscera of a person who died from arsenical poisoning, in the stomach 1.65 parts, in the large intestines 0.133, in the liver 0.105, in the lungs and heart 0.6, in the muscles 0.01 part, and in the brain only traces of the poison. (*Jour. Chem. Soc. Abst.*, Feb. 1884, 199.)

In an experiment in which a large dog was given 6.5 grammes of arsenious oxide with meat during a period of eight days, and was then killed, Profs. Johnson and Chittenden found in 100 grammes of the different organs the following quantities of absorbed arsenic: muscle, 0.2 milligramme; kidneys, 0.4; liver, 1.0 milligramme; whilst from the entire brain only a faint mirror was obtained. (*Amer. Chem. Jour.*, Nov. 1880, 332.)

In a judicial case examined by myself, in which a woman had suffered most violent symptoms of arsenical poisoning for some two or three days, and was then killed by blows upon the head, the largest quantity of absorbed arsenic was found in the liver; next the kidneys; less in the spleen; and still less in the brain. And in the instance of a large dog killed in twenty-six hours by twenty grains of arsenious oxide in two doses, we obtained from a given weight of the tissue the following proportions of arsenic: brain, 2 parts; kidneys, 9; liver, 17; spleen, 18 parts.

These instances, and many others that might be cited, clearly show that there is no exact uniformity in the distribution of the absorbed poison, but that as a general result, as already stated, the largest proportion will be found in the liver, kidneys, and spleen. Doubtless, as remarked by Prof. Johnson, the amount that may be found in any given organ or tissue will depend largely upon the ready solubility or otherwise of the form under which it was taken,

and the length of time the individual survived after taking the poison.

Failure to detect the Poison.—From experiments on animals Orfila concluded that, if there is no suppression of the natural secretions, absorbed arsenic is entirely eliminated from the living body in about fifteen days; and this view has been for the most part sustained by observations on the poisoned human subject. In an experiment upon a dog, Prof. Ludwig found a notable quantity of arsenic in the liver *forty days* after it had been taken. Independently of the action of absorption, the poison may, of course, be rapidly removed from the stomach and intestines by vomiting and purging. Thus, Dr. Taylor relates a case in which no arsenic was found in the stomach of an individual who died in *eight hours* after taking nearly *two ounces* of the poison. (*On Poisons*, 411.) So, also, instances are reported in which death took place within a few days after the poison had been taken, and none was found in any part of the body. According to the observations of Dr. Geoghegan, the liver usually receives its greatest quantity of absorbed arsenic in about fifteen hours after the poison has been taken, when the organ may contain as much as two grains of arsenic. A case is reported in which 2.77 grains of absorbed arsenic were recovered from the liver. (*Boston Med. and Surg. Jour.*, Feb. 1880, 150.) In the liver of a dog that had been under the influence of large doses of the poison for eight days and then died from its effects, we obtained only about 1–100th grain of arsenic. It must be remembered, however, that the poison may be entirely absent from the liver and yet be present in some of the other organs of the body. In a case related by Prof. Casper (*Forensic Medicine*), in which death occurred in twenty-four hours, arsenic, both in its solid state and in solution, was readily discovered in the contents of the stomach, but neither the blood nor the liver revealed its presence. And in a case recorded by Grohe and Mosler, in which a healthy child, two years old, swallowed a green arsenical paint and died from its effects in seventeen hours, arsenic was found in the vomited matters, but a chemical examination failed to reveal its presence either in the contents of the stomach and intestines, or in the spleen, liver, bile, or kidneys. (*Sydenham Soc. Rep.*, 1867, 435.)

Detection after long periods.—If arsenic be present in the body

at the time of death, the metal being indestructible, it may be recovered after very long periods. A case has already been mentioned in which we detected the poison, both in its absorbed state and in the stomach, in a body that had been buried seventeen months; and another in which it was found after the lapse of three and a half years. In a case quoted by Dr. Beck, the body had been buried for seven years. At this time the body was entire; the head, trunk, and shoulders had preserved their form and position, but the internal organs of the chest and abdomen were destroyed, and there remained only a mass of soft, brownish matter, which was deposited along the sides of the spine. A chemical examination of this matter, by MM. Ozanam and Idt, readily revealed the presence of arsenic. (*Med. Jur.*, ii. 594.) Prof. Charles H. Porter records a case in which he found about three grains of arsenic in a body that had been buried *eleven* years. In this instance the liver and lungs could still be recognized by their structure. (*Medico-Legal Contributions*, Albany, 1862.) Dr. J. W. Webster, of Boston, found four grains of arsenic in the body of a woman that had been buried in a vault for *fourteen* years. This seems to be the longest period yet recorded after which the poison has been discovered in the dead body.

Since arsenic exists in certain soils, it is sometimes objected, when the poison is detected in an exhumed body, that it may have been derived from the surrounding earth. This objection, however, has no practical force, unless only a very minute quantity of the poison has been discovered and the parts of the body examined were commingled with the earth. Under these circumstances, a portion of the earth may be separately examined for the poison. The quantity of arsenic present in arsenical soils, according to various observers, never exceeds a mere trace, and, in most instances at least, it can be extracted only by the stronger mineral acids.

Post-mortem Diffusion.—When the examination for *absorbed* arsenic is not made until some days after death, it may be a question whether any metal found in the more remote organs of the body was really carried there by absorption during life, or whether it found its way into the organ by simple *post-mortem imbibition* from some other organ or even from the alimentary canal.

And further, as first announced by Orfila long since, when the examination is not made until a still later period, it may be impossible, from chemical analyses alone, to determine whether any poison

found had been taken into the body *during life* or had been injected into the stomach or rectum *after death.*

A case involving this question was tried not long since in the State of Michigan. (*Jour. Amer. Med. Assoc.*, Aug. 1883; also, *Amer. Jour. Med. Sci.*, Oct. 1883, 599.) After the death of a lady, whose symptoms strongly pointed to arsenical poisoning, the husband, with a view of preserving the body for removal, claimed to have injected arsenic suspended in water into the mouth and rectum. One hundred and five days after death the body of the woman was disinterred, and the stomach and rectum placed in one jar, and a portion of the liver and one kidney in another. In the stomach and rectum together Prof. A. B. Prescott found about twenty grains of arsenious oxide, and from the analysis he calculated that the whole liver contained from six to fifteen grains, according to the size of that organ. Later the body was again disinterred, and the *brain* and a part of the *muscles* of the calf of the leg examined; but in these no arsenic was found.

The chief question asked the six experts was, "Granting that the arsenic was injected into the mouth and rectum in the manner claimed, could it reach the liver and other organs outside the alimentary canal?" On this question the experts were equally divided.

As bearing on this question, Drs. Vaughan and Dawson afterward made the following experiments:

About fifty grains (3.24 grammes) of arsenious oxide suspended in cold water were injected into the mouth and rectum of a dead musk-rat, and the animal was then buried. At the end of twenty-five days, the lungs were found to contain a much larger amount of the arsenic than the stomach, the larger portion of that injected having evidently passed down the trachea. Arsenic was found in the liver, heart, kidneys, and in the brain.

In the second experiment a cadaver was used, the body having been dead between two and three days when the injection was made. An unweighed quantity of arsenious oxide was injected into the mouth and rectum, and the body placed in a dry cellar for twenty-five days. At the end of this time diffused arsenic was found in the liver, spleen, heart, and again in the brain.

In a series of experiments on this subject by Mr. Frank S. Sutton, senior student in medicine, made in my own laboratory, the bodies of dogs killed by chloroform were employed. In each case three

grammes of arsenious oxide diffused in 50 c.c. of water were injected into the *stomach*, and an equal quantity of the oxide in 10 c.c. of water into the *rectum*. The body was then buried in the earth.

In the most protracted case of the series, in which the injection was made twenty-three hours after death, and the body was disinterred at the end of one hundred and two days, ten milligrammes (nearly 1–6th grain) of arsenious oxide were found in the *liver;* and the metal was readily detected in the *kidneys*, and in *one-fifth* of the final solution from the *brain*.

In three other cases in which the injections were made in from twenty-four and a half to twenty-six and a half hours after death, and the bodies examined at the end of seventy-four, forty-four, and eighteen days respectively, similar results were obtained, only that a gradually diminishing quantity of arsenic was found in these organs.

In a case in which the injection was made *six hours* after death, and the body examined at the end of *ten days*, arsenic was found in the liver and kidneys; and the *whole* of the final solution from the brain furnished a well-marked mirror by Marsh's method.

When the injection was made *ten minutes* after death, and the body examined at the end of *three days*, the final solution from the *brain* gave a well-marked stain in the reduction-tube of a Marsh apparatus, and satisfactory evidence of the presence of the metal in the liver and kidneys was obtained.

But when the injection was made *twenty-four hours* after death, and the body examined at the end of *three days*, the final solution from the brain furnished only the faintest trace of arsenic. The metal was present in very minute quantity in the liver; but it seemed to be entirely absent from the kidneys.

The last two mentioned experiments show, as might be expected, that if the injection is made very soon after death, the diffusion takes place more readily than when the injection is not made until some hours after death.

It has sometimes been held that so soon as decomposition of the body with evolution of sulphuretted hydrogen occurs, post-mortem diffusion will be arrested, the arsenic being converted into insoluble sulphide. But this view is contradicted by the results of the foregoing experiments, since even in the dogs exhumed at the end of three days yellow arsenious sulphide was present. According to J. Ossikovszky, as already mentioned, arsenious sulphide in the

presence of decomposing organic matter is itself after a time decomposed, the metal being oxidized to arsenious oxide and even arsenic oxide. The latter oxide is very diffusible, being extremely soluble.

Arsenic in Chemicals, Medicines, and Fabrics.—1. Since *sulphuric acid* and *metallic zinc* are very liable to be contaminated with arsenic, these substances should be carefully examined for this metal before being employed in judicial analysis. Both these substances are now more readily than formerly obtained free from arsenic. In every instance the analyst should determine the purity of the acid and the zinc for himself.

2. Arsenic may also be present in *hydrochloric acid* as an impurity, especially in what is known as the commercial acid. To test the acid, about 50 c.c., or two fluid-ounces, are treated with a saturated solution of stannous chloride and about half a volume of pure sulphuric acid, added small portions at a time, when if arsenic is present the mixture will soon present a brownish turbidity, and after a time yield a brown precipitate of the metal. In a sample of solution of *ferric chloride* F. W. Fletcher found about .06 per cent. of arsenic; and in others about .02 per cent., due to an impurity in the hydrochloric acid employed in the preparation of the mixture. (*New Remedies*, Dec. 1880, 371.) In this instance, however, the impurity may have been, in part at least, due to an impurity of the iron, since J. Mitteregger found in a sample of iron as much as 1.7 per cent. of arsenic. (*Amer. Chemist*, June, 1873, 471.)

For the purification of arsenical hydrochloric acid, A. Bettendorff advises to treat the acid with stannous chloride, allow the mixture to stand twenty-four hours, then separate the precipitate and distil the acid, collecting the first 1–10th separately, the remaining portion when distilled being entirely free from arsenic. (*Chem. News*, Oct. 1869, 189.)

3. According to Dr. Fresenius, crystallized commercial *sodium carbonate* sometimes contains a perceptible quantity of arsenic, due undoubtedly to the use of arsenical sulphuric acid in the manufacture of the salt. (*Chem. News*, Nov. 1869, 226.)

4. It has long been known that *basic bismuth nitrate*, or *subnitrate of bismuth*, is rarely free, at least as formerly prepared, from at least traces of arsenic, and sometimes this impurity is present in very notable quantity. Of six samples of the nitrate examined by Dr.

Gunning, every sample contained arsenic. (*Chem. News*, May, 1868, 260.) According to Prof. A. Stillé (*Therap.*, i. 166), .16 per cent. is the largest proportion of the metal that has been found in any specimen of the subnitrate presumed to be pure. Of fourteen samples of the salt examined by Prof. R. H. Chittenden (*Amer. Chem. Jour.*, Feb. 1882, 396), only *one* was found entirely free from arsenic; the other samples contained from 0.00435 to 0.07719 per cent. of arsenic, calculated as arsenious oxide, the average of the samples examined being 0.01302 per cent. Two cases of non-fatal poisoning by arsenical nitrate of bismuth are recorded in the *American Journal of the Medical Sciences* for Jan. 1874, 280.

In order to determine the extent of the absorption of arsenic from bismuth, when present as an impurity, Prof. Chittenden gave a dog during a period of five weeks 539 grammes (8318 grains) of the salt containing 66 milligrammes (slightly over one grain) of arsenic, the amount of arsenic given with the bismuth during the last three weeks being 2.38 milligrammes (1–27th grain) per day; the dog was then killed. Minute quantities of arsenic were found in the stomach and intestines, but only the *merest traces* in the liver, blood, kidneys, and muscles. Of the bismuth, only minute traces were found in the liver and the blood. From the experiments of the same observer, it would appear that arsenic when present in the bismuth salt is not (at least generally) in the form of arsenious oxide or any soluble form, since not a trace of arsenic, in a sample containing 0.0117 per cent., was extracted by large quantities of boiling water.

The arsenical impurity of bismuth nitrate was strongly urged by the defence in the case of *State of Virginia* vs. *Emily E. Lloyd*, charged with the murder of her child, aged about four years, with arsenic. (Leesburg, Va., 1872.) Bismuth nitrate with a little opium had been prescribed for the child on the second day of its illness, death taking place in about forty-eight hours after the symptoms first appeared, under excessive vomiting and purging, and great prostration. It did not clearly appear in evidence that the bismuth prescribed had really been administered. In the stomach of the deceased Prof. Tonry, of Baltimore, readily found arsenic; but as the coroner who had had charge of the jar containing the stomach died before the trial, the court, very properly, excluded the results of the analysis of this organ. At a second exhumation of the body made before the trial, Dr. Tonry took charge of the liver, spleen, and kidneys,

and found in these organs the equivalent of 86–100ths grain of arsenious oxide. Independent examinations, by Prof. J. W. Mallet and myself, of samples of the bismuth salt prescribed for the child, showed the presence of minute quantities of arsenic, my own results indicating 0.012 per cent., calculated as arsenious oxide. During the trial it was clearly shown that the prisoner had purchased a quantity of arsenic shortly prior to the death of the child. Moreover, the commonwealth claimed to have evidence tending to prove that previously three other children of the accused had died under very similar circumstances; this evidence, however, was not admitted. The woman was acquitted.

5. Arsenic is also not unfrequently present in minute quantity in *tartar emetic*, as an impurity. It is said that this salt when in well-formed crystals is always entirely free from arsenic. To examine tartar emetic for this impurity, Strohmeyer recommends to dissolve two grammes of the finely pulverized salt in four grammes of pure hydrochloric acid, of sp. gr. 1.124, then add to the solution thirty grammes more of the acid thoroughly saturated with sulphuretted hydrogen, and allow the mixture to stand. If arsenic is absent, the liquid remains perfectly colorless; but the presence of the slightest trace of the metal gives rise to a yellow coloration, and after a time a yellow precipitate of arsenious sulphide is formed. (*Chem. News*, Dec. 1869, 275.)

6. Arsenic is largely used in the arts in the preparation of certain pigments. Thus, *arsenite of copper*, or *Scheele's green*, and the *aceto-arsenite of copper*, known as *Schweinfurt green*, are largely employed for coloring wall-papers and artificial flowers; and *arsenic acid* is largely used in the manufacture of aniline colors, which, especially the various shades of red, often retain notable quantities of the metal. In nine wall-papers, of green and drab colors, examined by Mr. A. S. Parker (*Jour. Amer. Chem. Soc.*, July, 1880, 339), the proportion of arsenic, expressed as arsenic oxide, was found to vary from 0.216 grammes (3.3 grains) to 4.840 grammes (75 grains) per square yard. Two samples of green cambric contained, respectively per square yard, 4.000 and 3.879 grammes of arsenic.

For the separation of arsenic from fabrics of this kind, Mr. Parker advises to dissolve the arsenic from the material by hydrochloric acid, and treat the filtered solution with sufficient potassium hydrate to precipitate the copper. The filtered liquid is then acidu-

lated and treated with sulphuretted hydrogen, the precipitate oxidized with nitric acid, and heated on a sand-bath to expel the sulphuric acid and organic matter, the residue being weighed as arsenic oxide. When the arsenic is present as arsenite of copper, it may generally be dissolved out by dilute ammonia, forming a blue solution, which may be acidulated with hydrochloric acid and examined by Reinsch's test. This method, however, is not applicable in all cases, even when the arsenic exists as an arsenite. As a general method, Dr. Hills advises (*Boston Med. and Surg. Jour.*, Jan. 1881, 29) to cut the material into small pieces, moisten it with pure sulphuric acid, and heat till the mass is thoroughly charred. The pulverized mass is extracted with water, the liquid filtered, and then examined by Marsh's test.

Arsenic in Glass.—As is well known, arsenious oxide is frequently employed in the manufacture of glass, it being added chiefly for the purpose of oxidizing any iron present in the mixture to the state of ferric oxide. It is generally believed, and so stated in text-books, that after serving this purpose the arsenic is wholly volatilized, none of it remaining in the glass.

Recently, however, Dr. W. Fresenius found arsenic in each of three kinds of glass examined, even, in a sample of Bohemian glass, to the extent of 0.20 per cent. Moreover, he found that on strongly heating a mixture of potassium cyanide and sodium carbonate in a current of carbon dioxide, according to the method of Fresenius and Babo, in a tube of this kind, a very strong arsenical mirror was produced, due to the action of the fused mixture upon the glass. On placing the reducing mixture in a porcelain boat, so as to prevent contact with the glass, and repeating the experiment, no mirror was obtained, even on intense and prolonged heating. This author believes that the brown coloration sometimes observed in the glass in the application of Marsh's test is due to the presence of arsenic in the glass, and not, as is generally believed, to the action of lead. (*Zeits. Anal. Chem.*, 1883, 397 ; also, *Chem. News*, Sept. 1883, 147.)

Of two kinds of Bohemian glass, a sample of bottle-glass, and the glass of a beaker, examined in the University laboratory by Dr. J. Marshall and Mr. C. S. Potts, three of the samples were found to contain notable quantities of arsenic, one of the samples of Bohemian glass being entirely free from the metal. The arsenical Bohemian glass on being strongly heated, as in the method of Marsh,

acquired a brown coloration, but gave no mirror whatever. The other sample of this kind of glass failed to yield any coloration. The bottle-glass, on fusion, was found to contain 0.266 per cent., and the arsenical Bohemian glass 0.314 per cent., of metallic arsenic. The bottle-glass was of American manufacture; the other three kinds examined were from Thuringia. One gramme of a porcelain dish examined for arsenic failed to yield a trace of the metal.

A 10 per cent. solution of sodium hydrate, kept in a bottle of the above arsenical glass and examined daily, 20 c.c. at a time, acquired a distinct arsenical contamination at the end of three days. Arsenic was readily detected in a solution of this kind one month old; and the quantity was much increased at the end of five months. It should be borne in mind that commercial sodium hydrate may itself be contaminated with arsenic (*ante*, 89): in a sample of the hydrate claiming to be *chemically pure* examined in our own laboratory by Dr. Marshall, arsenic was present to the extent of 0.085 per cent., calculated as arsenious oxide; and in another sample a notable quantity of the metal was present.

A 10 per cent. solution of potassium hydrate, under the foregoing conditions, acquired a perceptible arsenical contamination in twenty-five hours. Solutions of ammonium hydrate and ammonium sulphide, and of various neutral reagents, kept in bottles of arsenical glass for long periods, failed to take up a trace of arsenic.

From the foregoing results it would appear that there would be little or no danger of arsenical glass yielding up any of the metal in the ordinary application of Marsh's test. Should it do so, this would be discovered in the preliminary examination prior to the addition of the suspected solution. In the method of Fresenius and Babo, however,—unless the glass was previously examined and found free from arsenic,—the substance with the reducing mixture should be placed in a porcelain boat, as advised by Fresenius, introduced into the tube and cautiously dried in the current of carbon dioxide before applying a strong heat to the mixture. All alkaline solutions and reagents capable of acting on glass, if preserved in glass bottles, should be carefully examined for arsenic before being employed in an analysis for this metal. The mineral acids have little or no action upon glass. Samples of concentrated sulphuric and hydrochloric acids that had been in bottles of strongly arsenical glass for over three years were found to be entirely free from the metal.

QUANTITATIVE ANALYSIS.—Arsenic, when in solution in the form of arsenious acid, is most readily estimated as arsenious sulphide. For this purpose the solution, free from organic matter and reducing substances, is acidulated with hydrochloric acid, and a slow stream of washed sulphuretted hydrogen gas passed through it, as long as a precipitate is produced; the mixture is then gently heated, and allowed to stand in a moderately warm place until the precipitate has completely subsided and the supernatant liquid has become perfectly clear. The precipitate is collected on a double filter (the two filters having been previously equipoised), and well washed, at first with water containing a little sulphuretted hydrogen, then dried at 100° C. (212° F.). The filters are now separated, placed on the opposite pans of the balance, and the excess of the one containing the precipitate determined.

One hundred parts by weight of dry arsenious sulphide correspond to 80,48 parts of pure arsenious oxide. A portion of the dried precipitate, heated in a reduction-tube, should completely volatilize, without charring or leaving any residue; otherwise it is not perfectly free from foreign matter. If organic matter or a reducing agent be present in the solution treated with sulphuretted hydrogen, the precipitate may consist largely, or even wholly, of free sulphur. Hence it is very important to determine the purity of the precipitate, especially when the absence of these agents has not been fully established.

When the arsenic exists as *arsenic acid*, it may be estimated as *ammonium-magnesium arsenate*, in the manner directed hereafter. By this method, however, the results are slightly too low, since the precipitate is very slightly soluble in the liquid from which precipitated. Arsenious acid is readily converted into arsenic acid by heating the hydrochloric acid solution with a little potassium chlorate, and maintaining the mixture at a moderate heat until the odor of chlorine has about disappeared.

The weight of a deposit of metallic arsenic obtained in the reduction-tube of Marsh's apparatus may be determined by separating the portion of the tube containing the deposit, by means of a fine file, and weighing it; the deposit is then expelled from the section of tube by heat or dissolved in nitric acid, and the clean and dried tube again weighed, when the loss of weight will represent the amount of metallic deposit present. One part of metallic arsenic corresponds to 1.32 parts of arsenious oxide.

3. Arsenic Oxide.—Arsenic Acid.

General Chemical Nature.—*Arsenic oxide*, or *arsenic anhydride*, known also as *anhydrous arsenic acid*, is a compound of two atoms of metallic arsenic with five atoms of oxygen, As_2O_5. In its pure state it is a white, odorless, deliquescent solid, of specific gravity 3.74. When exposed to a red heat, arsenic oxide fuses and is slowly dissipated, being resolved into arsenious oxide and free oxygen: $As_2O_5 = As_2O_3 + O_2$. When perfectly dry, arsenic oxide is only slowly soluble in water; but in its moist state it is very readily soluble in this menstruum.

When arsenic oxide dissolves in water, one molecule of the oxide assimilates the elements of three molecules of water, forming two molecules of *arsenic acid;* thus: $As_2O_5 + 3H_2O = 2H_3AsO_4$. Aqueous solutions of arsenic acid are colorless, and have a strongly acid reaction, quickly reddening litmus; this reaction is quite distinct in a solution containing only 1–10,000th of its weight of the free acid. When an aqueous solution of arsenic acid is treated with sulphurous oxide, known as sulphurous acid gas, the arsenic acid is reduced to arsenious acid, and the sulphurous oxide oxidized to sulphuric acid: $2H_3AsO_4 + 2SO_2 + 2H_2O = 2H_3AsO_3 + 2H_2SO_4$.

Arsenic acid, like common phosphoric acid, is tribasic, either one, two, or all three of the hydrogen atoms being replaceable by a metal. The *arsenates* of the alkalies are, for the most part, readily soluble in water; the other metallic arsenates are insoluble in water, but soluble in sulphuric, nitric, and hydrochloric acids. The arsenates of the fixed alkalies, containing two or three equivalents of metal for each molecule of acid, withstand a strong red heat without decomposition; but when they contain only one atom of metal, they are reduced to the bibasic or tribasic form, a portion of the acid being decomposed and evolved in the form of free oxygen and arsenious oxide. Under the action of heat arsenic acid displaces all volatile acids from their basic combinations.

In regard to its *physiological effects*, arsenic oxide appears, from the observations of several experimentalists, to be even more poisonous than arsenious oxide. As yet, however, there seems to be no instance of poisoning by it in its free state in the human subject. But several instances of poisoning by potassium arsenate and the sodium salt are reported. The symptoms observed in these cases

were much the same as those usually produced by arsenious oxide. The treatment and post-mortem appearances are also much the same.

Special Chemical Properties.—When a mixture of arsenic oxide or of an arsenate and sodium carbonate is heated on a charcoal support, in the inner blow-pipe flame, the arsenical compound is reduced and evolves the peculiar garlic-like odor of the vaporized metal. When arsenic oxide or any of its compounds is intimately mixed with a reducing agent, as potassium ferrocyanide, and the thoroughly dried mixture heated in a reduction-tube, it yields a sublimate of metallic arsenic, similar to that obtained under like circumstances from arsenious oxide.

When a drop of an aqueous solution of arsenic acid is allowed to evaporate spontaneously, the residue usually consists of a gummy mass; if, however, the evaporation has taken place very slowly, the acid is left chiefly in the form of long, slender, crystalline needles. This residue consists of two molecules of the acid with one molecule of water: $2H_3AsO_4$; H_2O. At 100° C. (212° F.) the water of crystallization is expelled; and at a heat little short of redness the arsenic acid is resolved into arsenic oxide and water, the latter being vaporized: $2H_3AsO_4 = As_2O_5 + 3H_2O$.

If the aqueous solution residue be moistened with water and exposed to sulphuretted hydrogen gas, it acquires a yellow color, due to the formation of sulphide of arsenic; when moistened with a yellow solution of ammonium sulphide and the mixture cautiously evaporated to dryness, it leaves a pale yellow residue, consisting of pentasulphide of arsenic, mixed with more or less free sulphur. Silver nitrate converts the arsenic acid residue into a red-brown deposit of tribasic silver arsenate, which seems to have a tendency to crystallize. Under this action of silver nitrate the 1–1000th of a grain of arsenic oxide yields a very good red-brown deposit, and 1–10,000th of a grain a quite distinct reddish-brown coloration.

In the following examinations in regard to the behavior of solutions of arsenic oxide, pure aqueous solutions of the free acid were employed.

1. *Sulphuretted Hydrogen.*

Normal solutions of arsenic acid, even when highly concentrated, fail to yield an *immediate* precipitate when treated with sulphuretted hydrogen gas; but sooner or later the mixture becomes turbid, and after some hours yields a light yellow precipitate, the color of which

is much lighter than that of the precipitate produced from solutions of arsenious acid. From solutions acidulated with hydrochloric acid the precipitate separates more promptly, but even under these conditions there is no immediate deposit. The precipitate, according to Wackenroder, consists of a mixture of free sulphur and arsenious sulphide, the sulphuretted hydrogen first reducing the arsenic acid to arsenious acid, and the latter then being decomposed and the metal precipitated as trisulphide: $2H_3AsO_4 + 5H_2S = 8H_2O + S_2 + As_2S_3$. The formation of the precipitate is much facilitated by a gentle heat.

The precipitate thus produced is insoluble in hydrochloric acid, but readily soluble to a clear and colorless solution in aqua ammoniæ, as well as in the sulphides and carbonates of that alkali. It is also soluble in the fixed caustic alkalies, and in their carbonates and sulphides; the fixed alkalies and their carbonates, however, leave a little free sulphur undissolved, which imparts to the solution a slight turbidity. If either of these solvent substances be present in the solution, the reagent will, of course, fail to produce a precipitate.

In the following experiments in regard to the limit of this test, *ten* fluid-grains of the arsenical solution, placed in a small test-tube, were acidulated with two drops of concentrated hydrochloric acid, and treated with a slow stream of washed sulphuretted hydrogen gas.

1. 1–100th solution ($=\frac{1}{100}$ grain of arsenic oxide) yields no immediate change, but in about five minutes the solution becomes slightly turbid, and in about five minutes more a strong, yellow turbidity appears; if the mixture be now allowed to stand for a few hours, a quite copious, pale yellow precipitate separates.

   A similar quantity of a *normal* solution of the acid, when treated with the reagent, becomes turbid in about the same time as an acidulated solution, but fails to yield a precipitate, even after standing many hours.

2. 1–1000th solution, when saturated with the sulphuretted gas, undergoes no perceptible change for about half an hour; the liquid then becomes turbid, and after several hours lets fall a good precipitate.

3. 1–10,000th solution: no perceptible change for some hours; after about eighteen hours a quite perceptible, yellowish precipitate has formed.

The arsenical nature of the precipitate produced by this reagent may be established by either of the following methods. *a.* When

the precipitate is boiled with diluted hydrochloric acid and a slip of bright copper-foil, the latter slowly receives a coating of metallic arsenic. *b.* If the precipitate be thoroughly dried and heated in a reduction-tube, it first fuses, then wholly volatilizes, yielding a viscid globular sublimate. The lower margin of this sublimate, while still warm, has a dark color, while the central portion appears red, and the upper margin yellow; when cool, the whole of the sublimate assumes a yellow color, which in the upper portion of the deposit is quite pale. *c.* When dried and heated in a reduction-tube, with a mixture of potassium cyanide and sodium carbonate, or with potassium ferrocyanide, it yields a sublimate of metallic arsenic.

On comparing the above results, obtained from solutions of arsenic oxide by sulphuretted hydrogen, with those obtained from solutions of arsenious oxide (*ante*, 265), it is obvious that the former oxide is much more slowly and less completely precipitated by the reagent than the latter. When, therefore, the poison exists in solution in the form of arsenic acid, before applying the reagent it should be reduced to arsenious acid, by saturating the solution with sulphurous oxide, and gently heating the liquid until the odor of the gas has entirely disappeared.

2. *Ammonio Copper Sulphate.*

This reagent produces in normal solutions of arsenic acid a greenish-blue, amorphous precipitate of copper arsenate, $CuHAsO_4$. The same precipitate is produced from solutions of neutral arsenates by copper sulphate alone, but this reagent fails to produce a precipitate in solutions of the free acid. The precipitate is readily soluble in nitric acid and in ammonia, also in excess of free arsenic acid. In its general deportment with reagents it is very similar to the corresponding precipitate produced from arsenious acid.

1. $\frac{1}{100}$ grain of arsenic oxide, in one grain of water, yields with the reagent a copious, greenish-blue precipitate, which after a time assumes a more distinctly green tint. Ten grains of the solution yield a bluish-green precipitate, which after a little time acquires a green color.
2. $\frac{1}{1000}$ grain: a good, bluish precipitate, destitute of a green tint. The precipitate from ten grains of the solution has a distinct greenish hue, which after a time becomes well marked.

This test, like the preceding, is much less satisfactory and deli-

cate when applied to solutions of arsenic acid than to those of arsenious acid.

3. *Silver Nitrate.*

Silver nitrate throws down from normal and neutral solutions of arsenic acid, when not too dilute, a reddish-brown precipitate of tribasic silver arsenate, Ag_3AsO_4. The precipitate is readily soluble in nitric acid, but nearly wholly insoluble in acetic acid; it is also freely soluble in ammonia, and sparingly soluble in ammonium carbonate and nitrate.

1. $\frac{1}{100}$ grain of arsenic oxide, in one grain of water, yields a quite copious precipitate, which aggregates into little masses, with a tendency to crystallize.
2. $\frac{1}{1000}$ grain: a copious, reddish-brown precipitate.
3. $\frac{1}{10,000}$ grain yields a dirty-white precipitate, which after a time assumes a reddish-brown tint. *Ten grains* of the solution yield a dirty reddish-brown precipitate, which after a time acquires a clear reddish-brown color.

The production of a reddish-brown precipitate by this reagent is quite peculiar to arsenic acid.

Ammonio silver nitrate produces, in solutions of arsenic acid, much the same results as the silver salt alone, as above described.

4. *Reinsch's Test.*

When a solution of arsenic acid or of an arsenate is strongly acidulated with hydrochloric acid and boiled with a slip of bright copper-foil, metallic arsenic is slowly deposited upon the copper, forming an iron-gray or steel-like coating, the appearance depending on the thickness of the deposit. Without the addition of the hydrochloric acid the metallic deposit fails to appear. The arsenical nature of the deposit may, of course, be shown in the same manner as heretofore pointed out in the consideration of this test for the detection of arsenious acid.

1. $\frac{1}{100}$ grain of arsenic oxide, in one grain of water, when acidulated with hydrochloric acid, and heated to about the boiling temperature with a mere fragment of copper-foil, yields, after a time, a very good metallic deposit upon the copper.
2. $\frac{1}{1000}$ grain: after a time a quite good deposit.
3. $\frac{1}{10,000}$ grain imparts only a slight tarnish to the copper, even

after prolonged heating, the evaporated liquid being frequently renewed.

It will be observed, on comparing the above results with those obtained from solutions of arsenious oxide, that the metal is much less completely separated by the test from solutions of arsenic oxide than from arsenious oxide.

5. *Ammonium Magnesium Sulphate.*

This reagent may be prepared by precipitating a solution of pure magnesium sulphate by ammonia, and then adding sufficient ammonium chloride to redissolve the precipitate; or, according to Fresenius, by dissolving one part of crystallized magnesium sulphate and one part of ammonium chloride in eight parts of water and four parts of solution of ammonia, allowing the mixture to stand at rest for some days, and then filtering.

Solutions of free arsenic acid, and of neutral arsenates, yield with the reagent a white, crystalline precipitate of ammonium magnesium arsenate, which contains six molecules of water of crystallization, the formula being $MgNH_4AsO_4,6H_2O$. The precipitate is readily soluble in nitric, hydrochloric, and acetic acids, also in excess of free arsenic acid, but only very sparingly soluble in ammonia and in ammonium chloride. The reagent fails to produce a precipitate in solutions of arsenious oxide.

1. $\frac{1}{100}$ grain of arsenic oxide, in one grain of water, yields a copious, white, amorphous precipitate, which immediately begins to crystallize, and in a little time becomes converted into a mass of plumose crystals, Plate V., fig. 1.
2. $\frac{1}{1000}$ grain: no direct precipitate, but almost immediately crystals begin to separate, and very soon there is a copious deposit of crystals, having much the same forms as those illustrated under 1.
3. $\frac{1}{5000}$ grain: almost immediately a granular cloudiness appears, followed in a little time by crystals; after several minutes there is a quite good crystalline deposit.
4. $\frac{1}{10,000}$ grain: in a very little time a granular turbidity, and after some minutes a satisfactory precipitate, consisting principally of small crystalline plates.

The reagent also produces a similar crystalline precipitate in solutions of phosphoric acid. The true nature of the arsenical crystals

may be readily established by dissolving the precipitate in large excess of hydrochloric acid and boiling the solution with a slip of bright copper-foil, when the latter will receive a coating of metallic arsenic.

Lead acetate throws down from solutions of free arsenic acid and of alkaline arsenates a white, curdy precipitate of tribasic lead arsenate, $Pb_3 2AsO_4$. One grain of a 1–100th solution of the oxide yields a quite copious precipitate; the same quantity of a 1–1000th solution yields a very good precipitate; and a 1–10,000th solution becomes quite turbid. It need hardly be remarked that this reagent also produces white precipitates in solutions of many other acids.

Under the action of zinc and diluted sulphuric acid, in a Marsh's apparatus, arsenic acid undergoes decomposition, with the production of arsenuretted hydrogen, much in the same manner as arsenious acid.

Solutions of arsenic acid, unlike those of arsenious acid, fail to reduce acid potassium chromate; nor do they give rise to red copper suboxide, when boiled with caustic potash and copper sulphate.

Quantitative Analysis.—Arsenic oxide, when in solution, may be estimated in the form of ammonium magnesium arsenate. The solution is treated with excess of a clear mixture of magnesium sulphate, ammonia, and ammonium chloride, prepared in the manner already described, and then allowed to stand in a cool place for from twelve to twenty-four hours, in order that the precipitate may completely separate. The precipitate is then collected on a filter of known weight, washed with water containing a little ammonia, dried at 100° C. (212° F.) as long as it loses in weight, and its weight then noted. The dried precipitate, if pure, will now consist of $2MgNH_4AsO_4; H_2O$, every 100 parts of which, by weight, correspond to 60.53 parts of arsenic oxide, 52.1 of arsenious oxide, or 39.47 of metallic arsenic.

Instead of drying the precipitate until it is constant in weight, in the manner just directed, it may be carefully transferred from the filter to a small weighed porcelain crucible and then ignited; the filter is burned separately, the ash added to the cooled contents of the crucible, and the whole moistened with nitric acid and again heated to redness. The precipitate will thus be converted into *magnesium*

pyro-arsenate, which has the composition $Mg_2As_2O_7$, and contains 48.38 per cent. of metallic arsenic.

Arsenic oxide may also be estimated by first reducing it to arsenious oxide, by means of sulphurous oxide, and then precipitating the metal as arsenious sulphide, by sulphuretted hydrogen. One hundred parts by weight of thoroughly dried arsenious sulphide correspond to 93.5 parts of anhydrous arsenic oxide.

CHAPTER VI.

MERCURY.

Properties.—In its uncombined state, at ordinary temperatures, *mercury*, or *quicksilver*, as it has been named, is a liquid metal having a silver-white color, high metallic lustre, and a density of 13.595; its atomic weight is 200. Mercury is the only metal that is fluid at ordinary temperatures. At —39.4° C. (—39.6° F.) it solidifies to a crystalline, ductile mass; and at about 350° C. (662° F.) it boils, being dissipated in the form of a colorless, transparent vapor, the specific gravity of which is 6.976. Water has no action on the metal in its pure state. Diluted nitric acid dissolves it to mercurous nitrate; the hot concentrated acid readily dissolves it to mercuric nitrate, with evolution of nitrous fumes. Hydrochloric acid has no action upon the metal, but boiling sulphuric acid readily converts it into mercuric sulphate, with evolution of sulphurous oxide.

Physiological Effects.—Many instances are reported in which large quantities of metallic mercury, even in some instances amounting to some pounds, were taken into the body without producing any deleterious effects. If, however, the metal, after being swallowed, becomes oxidized, as is sometimes the case, it may produce active symptoms. A case in which about four ounces and a half of quicksilver, given to procure abortion, produced serious symptoms, has been reported by Sir G. Duncan Gibb. (*Amer. Jour. Med. Sci.*, July, 1873, 280.) When inhaled in the form of *vapor*, mercury may give rise to serious results, as has not unfrequently been witnessed in those engaged in mining the metal, and others exposed to its fumes. In a case of this kind reported by M. Ferrand, a woman exposed to the fumes experienced violent effects, which continued for a month or longer. (*Med.-Chir. Rev.*, April, 1869, 547.)

Combinations.—Mercury readily unites with most of the non-

metallic elements. With oxygen it combines in two proportions, forming the black, or suboxide, known also as mercurous oxide, Hg_2O, and the monoxide, red oxide, or mercuric oxide, HgO. These oxides readily unite with acids, forming salts. The metal also unites with sulphur in two corresponding proportions: the subsulphide, Hg_2S, has a black color, so also has the monosulphide, HgS; by sublimation the latter compound acquires a beautiful red color, under which form it is commonly known as *vermilion*. Mercurous iodide, Hg_2I_2, has a dingy green color, while mercuric iodide, HgI_2, has a brilliant scarlet hue. The compounds of mercury most frequently employed for medicinal purposes are the two chlorides, known at present as mercurous chloride, or calomel, Hg_2Cl_2, and mercuric chloride, or corrosive sublimate, $HgCl_2$.

All the compounds of mercury are more or less poisonous; but of these, corrosive sublimate is one of the most active, and, in a medico-legal point of view, much the most important.

Corrosive Sublimate.

Composition.—*Corrosive sublimate* consists of one atom of mercury combined with two atoms of chlorine, its formula being $HgCl_2$. Some confusion has existed in regard to the nomenclature of the chlorides of mercury, since formerly the atomic weight of the metal was assumed to be 100, whereas at present it is regarded as 200. As met with in the shops, corrosive sublimate is usually either in the form of a white, amorphous powder, or of semi-transparent crystalline masses; but occasionally it is found in the form of well-defined crystals.

Symptoms.—The effects of corrosive sublimate, when swallowed in poisonous quantity, are a nauseous, metallic taste, with a sense of heat and constriction in the mouth and throat; nausea, and pain in the stomach, attended with violent vomiting and retching, the matters ejected being sometimes of a bilious character and containing blood; pain throughout the abdomen, which generally becomes swollen and tender to the touch; severe purging, sometimes of bloody matters; great anxiety; flushed countenance; impaired or difficult respiration; small, frequent, and contracted pulse; cold perspirations; intense thirst; scantiness or entire suppression of urine; cramps in the extremities; stupor; and sometimes death is ushered in with convulsions.

Such are the symptoms usually produced by large doses of this poison; but they are subject to considerable variation. The vomiting and purging, as well as the pain in the stomach and bowels, may cease for a time, and afterward return with increased violence. Instances are also reported in which purging and pain in the abdomen were even entirely wanting. In some instances, on account of the local action of the poison, the lining membrane of the mouth and the surface of the tongue present a white appearance. In protracted cases, inflammation of the mouth and salivation usually supervene.

Among the more prominent differences usually observed between the symptoms of corrosive sublimate poisoning and those occasioned by arsenious acid, Dr. Christison mentions the following: 1. The symptoms of the former generally begin much sooner, the irritation in the throat often manifesting itself during the act of swallowing, and that in the stomach either immediately or within a few minutes; 2. Its taste is much more unequivocal and strong; 3. The sense of acridity along the throat and in the stomach is much more severe; and, 4. Blood is more frequently discharged by vomiting and purging.

The following case, related by Devergie and quoted by Dr. Christison, well illustrates the usual course of acute poisoning by this substance. A woman swallowed three drachms of corrosive sublimate in solution. She was soon afterward seized with vomiting, purging, and pain in the abdomen. In five hours the skin was cold and clammy, the limbs relaxed, the face pale, eyes dull, and the expression that of horror and anxiety. The lips and tongue were white and shrivelled, and there were violent fits of pain and spasm in the throat whenever an attempt was made to swallow liquids; also burning and pricking along the gullet; frequent vomiting of mucus and bilious matters, with burning pain in the stomach and tenderness of the epigastrium on the slightest pressure; and profuse purging, with tenesmus. The pulse was almost imperceptible, and the breathing much retarded. In eighteen hours, these symptoms still continued without any material change; but the limbs were then insensible. In twenty-three hours, the patient died in a fit of fainting, the mind having remained clear up to the time of death.

In a case reported by Dr. J. W. Ogle (*St. George's Hosp. Rep.*, 1868, 238), a man of intemperate habits swallowed a tablespoonful, it was said, of corrosive sublimate in a cup of vinegar. Within an hour after taking the poison the patient began to suffer severe pain

in the œsophagus and epigastric region; and there was vomiting and purging, the matters vomited and passed by the bowels being mixed with blood. When admitted to the hospital, his face was of a dusky leaden color; the expression very anxious; and there were tremors of the lips and limbs. There was no pulse, the skin was cold, and articulation was difficult. The vomiting and purging continued. On the following day he was better, the purging was less, and there was no pain; the pulse had become natural. Later, however, hiccough supervened, and the purging returned. Collapse set in, and the patient died sixty hours after taking the poison. Dr. Ogle relates another case in which about two drachms of the poison proved fatal on the sixth day. In this instance there was a paralytic condition of the upper eyelid (ptosis) and facial paralysis.

Dr. H. M. Post, of St. Louis, reports a case in which sixty grains of the poison were given by mistake to a young woman convalescing from intermittent fever. (*Boston Med. and Surg. Jour.*, Nov. 1879, 781.) Although there was speedy and free vomiting, this was continued by the administration of large quantities of milk and an emetic. Some three or four hours after the poison was given there was an abundant discharge of urine, and several evacuations from the bowels. The patient suffered little pain, and the following day her recovery seemed almost certain. The third day, however, she was very weak, vomiting recurred, and she seemed sinking. The symptoms were suppression of the urine, insomnia, and loss of appetite; only after some days was any abdominal tenderness developed. On the evening of the sixth day the patient died in convulsions.

In a very protracted case, reported by Dr. Vigla, the following symptoms were observed. A man, aged twenty-seven years, swallowed, in a state of solution, about fifty grains of corrosive sublimate. At once there occurred a strong metallic taste, constriction of the throat, nausea, and vomiting; but no severe pain. The vomited matters at first consisted of food, then of a serous fluid. An emetic was administered, and afterward milk and white of egg. On the following day there was more intense pain and irritation of the throat, coming on in paroxysms; convulsive cough, expectoration of bloody mucus, and much suffering. Enteritis also developed itself, with violent colic, tenesmus, and frequent slimy and bloody evacuations. On the third day there was great inflammation of the mucous

membrane of the throat and mouth, œdema of the palate and gullet, pseudo-membranous separation from the inflamed parts, and salivation; the intelligence was somewhat restored. The pulse was eighty-six; the urine normal. Up to the twelfth day, all inflammatory symptoms gradually subsided; but from that time great prostration of the powers of life and mercurial cachexia were presented. On the fifteenth day, ecchymosis upon the skin, irregular action of the heart, hiccough, albuminuria, and great irritability of the whole body were present. The man died on the sixteenth day, without any convulsion or struggle, in a state of extreme exhaustion. (*Med.-Chir. Rev.*, Oct. 1860, 380.)

In poisoning by frequently repeated small doses of corrosive sublimate, or *chronic poisoning*, as it is termed, the following symptoms are usually observed: a coppery taste in the mouth, loss of appetite, offensive breath, tenderness of the gums, pains in the stomach and bowels, nausea, inflammation and ulceration of the salivary glands, swelling of the tongue, increased flow of saliva, hot skin, quick pulse, and great muscular debility. It is well known that some persons are much more susceptible than others to the action of mercurial compounds. In a case cited by Dr. Christison, two grains of calomel caused ptyalism, extensive ulceration of the throat, exfoliation of the lower jaw, and death.

The *external application* of corrosive sublimate has not unfrequently been followed by fatal results. Two children, aged seven and eleven years respectively, had an ointment composed of one part of corrosive sublimate to four parts of tallow rubbed over the scalp, for the cure of scald-head. Extreme suffering almost immediately ensued, and in forty minutes they were completely delirious. There was excessive vomiting, great pain in the bowels, with purging and bloody stools, and, in one instance, complete suppression of urine: there was no ptyalism. Death ensued in one instance on the seventh, and in the other on the ninth, day. (Wharton and Stillé, *Med. Jur.*, 535.) In an instance quoted by Orfila, the application of powdered corrosive sublimate to the breast of a woman affected with an ulcerated cancer caused intense pain in the part, nausea, bloody vomiting, convulsions, and death on the following morning.

Dr. Leiblinger relates an instance in which three persons were found dead in their beds who some days before rubbed their bodies over with an ointment made from quicksilver, as a cure for itch.

Chemical analyses of the visceral organs of the bodies showed the presence of large quantities of mercury. (*Med.-Chir. Rev.*, Jan. 1872, 270.)

Period when Fatal.—The fatal period in acute poisoning by corrosive sublimate is subject to considerable variation; but on an average, perhaps, death takes place in about twenty-four hours. In an instance in which three children were accidentally poisoned by this substance, dispensed by mistake for calomel, the eldest, aged seven years, took eighteen grains, and died in *three hours;* the youngest, aged about two years, took six grains, and died in *eleven hours;* while the second, aged three years, received twelve grains, and apparently recovered from the immediate effects of the poison, but died with secondary symptoms on the *twenty-third day.* (*Med.-Chir. Rev.*, April, 1835.) In a case recorded by Dr. Taylor (*On Poisons,* 462), a man died from the effects of an unknown quantity of the poison in less than *half an hour.* This is the most rapidly fatal case yet reported.

In regard to protracted cases, Dr. Beck cites an instance in which death did not occur until the eighth day; and another in which a man took about six or eight grains of the poison, and life was prolonged until the twelfth day. (*Med. Jur.*, ii. 620.) In a case reported by Dr. Coale, death took place on the eleventh day; and in another, by Dr. Jackson, on the thirteenth day. (Wharton and Stillé, *Med. Jur.*, 534.) In Dr. Vigla's case, already cited, death was delayed until the sixteenth day.

Fatal Quantity.—That the same effects are not always produced by equal quantities of corrosive sublimate is well illustrated in the cases of the three children just cited, in one of whom *six grains* of the poison caused death in eleven hours, whilst in another *twelve grains* did not prove fatal until the twenty-third day. In Dr. Coale's case, *ten grains* of the poison, dispensed by mistake for calomel, "were mixed and partially swallowed, but the great distress it caused produced ejection of much of it from the stomach." (*Amer. Jour. Med. Sci.*, Jan. 1851, 47.) This case is also remarkable in that during the eleven days the man survived after taking the dose there was entire suppression of urine. A case has also just been cited in which *six* or *eight* grains proved fatal to an adult.

Dr. Kobryner reports a case in which a young man under treatment for syphilis took *one-third of a grain* of corrosive sublimate in

two pills. He soon experienced intolerable burning pain in the stomach and abdomen, and vomiting. His pulse became small, the extremities cold, and his face pinched. After ten hours, the symptoms began to diminish, the patient finally recovering. (*Med. Times*, Phila., Nov. 1878, 60.)

On the other hand, several instances are reported in which persons recovered after having taken from half a drachm to two drachms of the poison; and Dr. Beck quotes an instance in which recovery took place after six drachms, in solution, had been swallowed. The writer just mentioned also cites a case, reported by Dr. Budd, in which a female took *an ounce* of the poison, and, after suffering the usual severe symptoms, entirely recovered. So, also, Dr. Taylor cites an instance mentioned by Dr. Booth, in which recovery followed after a similar quantity had been taken. It is but proper to add that in most, if not in all, of these cases of recovery there was early vomiting.

Treatment.—Of the various antidotes that have been proposed in poisoning by corrosive sublimate, albumen, in the form of white of egg, seems to be much the most efficient. Orfila, who first suggested this antidote, employed it with complete success in experiments on poisoned animals; and it has in several instances been, at least apparently, the means of saving life in the human subject. It should be given in large quantity, and its administration speedily followed, if necessary, by the exhibition of an emetic. According to Dr. Peschier, the white of one egg is required to neutralize four grains of the poison. Dr. Taddei strongly advised as an antidote the use of wheat flour, or gluten. This remedy has been successfully administered to animals, and has been resorted to with apparent success in the human subject. The free exhibition of milk has been highly recommended.

Dr. Buckler, of Baltimore, in 1842, proposed the use of a mixture of gold-dust and iron-filings, and adduced some experiments on animals in support of its efficacy; but these results were not confirmed by the experiments of Orfila. (*Toxicologie*, i. 687.) More recently, Dr. C. Johnston, of Baltimore, exhibited this mixture to a gentleman who had swallowed eighty grains of corrosive sublimate, and the patient recovered. (*Amer. Jour. Med. Sci.*, April, 1863, 340.) Since, however, in this case, previous to the administration of the gold mixture, which was not exhibited until about twenty-five

minutes after the poison had been taken, there had been violent and almost incessant vomiting for about fifteen minutes, and a mixture of white of egg and milk had been freely given, it is by no means certain that the alleged antidote had any part whatever in the recovery of the patient.

Among the other antidotes that have been advised for this poison may be mentioned stannous chloride (protochloride of tin), iron filings either alone or mixed with zinc, the hydrated sulphides of iron, the alkaline carbonates, and meconic acid and its soluble salts. Neither of these substances, however, possesses any advantage over those mentioned above, and in fact some of them seem to be entirely inert; moreover, neither of them is as likely to be at hand as either white of egg, flour, or milk.

Post-mortem Appearances.—The lining membrane of the mouth, fauces, and œsophagus is frequently more or less inflamed and softened; but cases are reported in which these parts were found in a perfectly normal condition. The action of this poison upon the stomach and bowels is generally much greater than that usually caused by arsenic. The coats of the stomach are often more or less corroded and softened; and its internal surface has presented a dark, ulcerated appearance. In a case cited by Dr. Christison, in which the patient survived thirty-one hours, the coats of the stomach were perforated. The intestines, especially the colon and rectum, often present signs of violent inflammatory action. This condition has been observed in cases in which the stomach was found but little affected. The urinary organs also are often much inflamed, and the bladder greatly contracted and nearly or altogether empty. An instance is related in which the bladder was reduced to the size of a walnut; and another, that of a child, in which this organ was no larger than a marble.

In the two cases of the three children already mentioned, which proved fatal in three and eleven hours respectively, the mucous membrane of the mouth, pharynx, and œsophagus was found, in several places, softened, white, and could be easily detached by the handle of the scalpel. The mucous surface of the stomach and bowels exhibited patches of acute inflammation, and here and there of partial erosion; at these places its color was of a deep brown, or of an eschar-like hue. On the inner surface of the left ventricle of the heart, in the elder child, there were observed two patches of

distinct ecchymosis, caused by the effusion of blood between the investing serous membrane and the muscular tissue. In the younger child, also, a similar appearance, but less distinctly marked, was found. No other appearances are mentioned in the description of these cases.

In a case related by Dr. H. Williams (*Am. Jour. Med. Sci.*, Jan. 1851, 79), in which thirty grains of the poison proved fatal to an adult on the third day, the following appearances were observed twenty-five hours after death. The stomach was contracted for the extent of about two inches, at its middle portion, into the form of a dumb-bell. It contained a small quantity of bright yellow fluid having the consistency of thin gruel. Its larger and smaller curvatures presented patches of dotted injection, of a bright crimson tint; and the mucous membrane was a little softened in the neighborhood of the most vivid red patches. Patches of beautifully arborescent vascularity were also observed at intervals along the whole extent of the small intestines; the large intestines were healthy. The bladder was contracted, and contained about a drachm of turbid urine. The other organs of the body were healthy.

In the case reported by Dr. Ogle, fatal in sixty hours, the lungs were emphysematous, and all the cavities of the heart contained large blood-coagula. The upper part of the œsophagus was natural, but the lower part was of a rusty color, and nearer to the stomach it was corroded. The mucous membrane of the great curvature of the stomach presented many dark lines, showing the charring effect of the poison on the prominent folds. The upper portion of the duodenum was of a rusty color, and beyond this it was soft and swollen. Below this point the small intestine was covered throughout with an adherent fine, white, powdery deposit. The brain was watery, and the subarachnoid spaces contained more than usual fluid.

In Dr. Post's case, fatal on the sixth day, twenty-seven hours after death, there being no signs of decomposition, there was found marked congestion of the lungs, and the heart was relaxed and flabby; the œsophagus and cardiac extremity of the stomach were very much congested, but there were no signs of ulceration. The alimentary tract appeared more or less congested, especially the small intestines. The kidneys were much increased in size, and were heavier than normal; the bladder was empty. The post-mortem plainly indicated uræmia, produced by congestion of the kidneys.

Chemical Properties.

General Chemical Nature.—Corrosive sublimate crystallizes, without water of crystallization, in the form of colorless, transparent, rhombic prisms. Its specific gravity has been variously stated at from 5.2 to 6.5. It has an exceedingly styptic, nauseous, metallic, and persistent taste. When heated to a temperature of 265° C. (509° F.), it fuses to a colorless liquid, which boils at about 295° C. (563° F.), evolving an extremely acrid and poisonous vapor. If the vapor be received upon a cold surface, it frequently condenses in the form of white crystalline needles.

Corrosive sublimate is readily decomposed by the fixed alkalies, forming a chloride of the alkali and oxide of mercury. Cold sulphuric acid fails to decompose or dissolve it, but it is somewhat soluble, without decomposition, in nitric and hydrochloric acids. When in aqueous solution, it is readily decomposed and precipitated by various vegetable and animal principles, such as albumen, fibrin, casein, gluten, and tannic acid. Hence the utility of these substances, as antidotes, in poisoning by this salt.

Solubility. 1. *In Water.*—The solubility of corrosive sublimate in water, at the ordinary temperature, has been variously stated at from nine to twenty parts of the fluid. According to our own experiments, when the pure, powdered crystallized salt is digested with ten times its weight of pure distilled water at a temperature of about 15.5° C. (60° F.), with occasional agitation, for twenty-four hours, the solution then filtered, and the filtrate cautiously evaporated to dryness, it leaves a residue indicating that one part of the salt had dissolved in 13.30 times its weight of the liquid.

According to most observers, the salt is soluble in less than three times its weight of boiling water. From these statements it is obvious that the quantity of the poison that may be taken up in solution by water will in a great measure depend upon the temperature of the latter.

2. *In Alcohol.*—When the powdered salt is agitated for some minutes, at the ordinary temperature, with two parts of alcohol of specific gravity 0.800 (= 98 per cent.), the solution filtered, and evaporated to dryness, the residue indicates that one part of the poison had dissolved in 2.47 parts of the liquid.

On digesting the powdered salt with five parts of *common whiskey*

for twenty-four hours, at the ordinary temperature, with frequent agitation, one part of the former required *fifteen* parts of the latter for solution.

3. *In Absolute Ether.*—When powdered corrosive sublimate is digested, with frequent agitation, for twenty-four hours, with five parts of absolute ether, at a temperature of about 15.5° C. (60° F.), one part of the salt dissolves in 8.8 parts of the menstruum. The salt is much more freely soluble in ordinary *commercial ether*, this liquid usually taking up about one-third of its weight of the poison.

By taking advantage of the solubility of corrosive sublimate in ether, the salt may be separated from its aqueous solution, or from organic mixtures. If one grain of the mercury compound be dissolved in one hundred grains of pure water, and the solution agitated for several minutes with an equal volume of commercial ether, the latter withdraws from the water 0.67 of a grain of the salt. According to M. Karls, the presence of camphor very much increases the solvent power of both ether and alcohol for corrosive sublimate.

4. *In Chloroform.*—Corrosive sublimate is only very sparingly soluble in chloroform. When the powdered salt is occasionally agitated during twenty-four hours with twenty parts of this liquid, at the ordinary temperature, one part of the salt requires seventeen hundred parts of the fluid for solution.

Of Solid Corrosive Sublimate.

In its solid state, corrosive sublimate may be identified by a variety of reactions.

1. When a small portion of the salt is moistened with a drop of a solution of *potassium iodide*, it assumes a bright scarlet color, due to the formation of mercuric iodide, which is soluble to a colorless solution in excess of the potassium compound. This reaction is extremely delicate, and peculiar to the mercuric combinations. The residue obtained from the evaporation of one grain of water containing the 1–1000th of a grain of corrosive sublimate, when moistened with the reagent, acquires a fine scarlet color; the residue from the 1–10,000th of a grain assumes a distinct yellow hue, and soon dissolves.

2. If a drop of a strong solution of *potassium iodide* be placed

on a piece of bright *copper*, and a small quantity of corrosive sublimate added, the latter undergoes decomposition, and the copper becomes stained with a deposit of metallic mercury, which when rubbed with a soft substance, as the end of the finger, assumes a bright silvery apppearance. This reaction will manifest itself with the least visible quantity of the mercurial compound. The dried stain is readily dissipated by heat. If in this experiment the potassium iodide solution be substituted by a drop of hydrochloric acid, the same metallic deposit takes place, and the reaction is equally delicate.

3. When corrosive sublimate is moistened with a few drops of a solution of *stannous chloride*, it slowly assumes a gray color, and finally becomes nearly black, from the separation of metallic mercury. In this reaction the mercurial compound yields up the whole of its chlorine to the tin, converting the latter into tetrachloride of tin.

4. If the salt be treated with a few drops of a solution of *ammonium sulphide*, it quickly acquires a yellow color, which in a little time changes to black, due to the formation of sulphide of mercury. This transition of color is peculiar to mercuric combinations of the metal.

5. When touched with a strong solution of *caustic potash* or of *soda*, it immediately assumes a yellow or brownish-yellow color, due to the production of mercuric iodide. This reaction serves to distinguish corrosive sublimate from calomel, which is blackened by the reagent, due to the formation of mercurous oxide. Calomel is also blackened by caustic ammonia, whereas the color of corrosive sublimate remains unchanged.

6. When a small quantity of corrosive sublimate is heated in a reduction-tube, it volatilizes unchanged, and recondenses in the cooler portion of the tube, usually in the form of groups of crystals of the forms illustrated in Plate V., fig. 2. The exact forms of these crystals, however, will depend in great measure upon the quantity of the salt employed: the most perfect crystals are obtained by using only a very minute portion of the salt; when a comparatively large quantity is employed, the sublimate is in the form of a dense crystalline mass, destitute of any distinct crystals.

In applying this test, the analyst should bear in mind that ammonium salts, oxalic acid, and arsenious oxide will also, like corro-

sive sublimate and certain other compounds of mercury, completely volatilize, with the production of a white sublimate. The sublimate from arsenious oxide, however, is in the form of octahedral crystals, whereas that from corrosive sublimate is never in the octahedral form; moreover, the former substance does not fuse before volatilizing. The sublimates from oxalic acid and ammonium salts may closely resemble that from the mercurial compound, but the latter is readily distinguished from these, as well as from all other volatile white powders, in that when touched with a solution of potassium iodide it assumes a bright scarlet color.

7. When a small quantity of perfectly dry corrosive sublimate is intimately mixed with several times its volume of recently ignited sodium carbonate, and the mixture heated in a reduction-tube, the heat being very gradually increased, it yields a globular sublimate of metallic mercury; at the same time an equivalent quantity of sodium chloride is formed and remains in the residue. The reaction in this case is expressed as follows: $HgCl_2 + Na_2CO_3 = 2NaCl + Hg + CO_2 + O$. This reaction will manifest itself with the least visible quantity of the corrosive salt, at least if the operation be conducted in a very narrow or contracted tube; it must be remembered, however, that the production of the metallic sublimate is common to all the compounds of mercury.

When the sublimate thus obtained is examined under a low power of the microscope, it will be found to consist of minute, opaque, spherical globules, which under incident light have an exceedingly brilliant, metallic lustre. These characters readily distinguish the mercurial from all other sublimates. The presence of the chlorine in the sodium chloride, resulting from the decomposition of the corrosive sublimate, may be shown by dissolving the saline residue in a little warm water, acidulating the solution with nitric acid, and then adding a little silver nitrate, when the chlorine will be thrown down as white chloride of silver, which is insoluble in nitric acid but readily soluble in ammonia. Similar results would be obtained if the substance submitted to examination was calomel; but the insolubility of the latter in water readily distinguishes it from corrosive sublimate. Before resorting to this method of reduction in the examination of a suspected substance, the operator should satisfy himself that the sodium carbonate about to be employed is perfectly free from chlorine.

Of Solutions of Corrosive Sublimate.

Pure aqueous solutions of corrosive sublimate are colorless, and, when not very dilute, feebly redden litmus-paper. The nauseous metallic taste of the salt is well marked, even in very highly diluted solutions. On cooling, hot concentrated solutions throw down the excess of the salt in its crystalline state. When a drop of a tolerably strong solution is allowed to evaporate spontaneously, the residue usually consists of long, transparent, crystalline needles and prisms; but from more dilute solutions it is generally in the form of a confused crystalline film. The crystallization of the salt is readily interfered with by the presence of organic matter.

In the following investigations in regard to the chemical behavior of solutions of corrosive sublimate, pure aqueous solutions of the salt were employed. The fractions indicate the fractional part of a grain of the anhydrous salt present in one grain of the liquid; and the results, unless otherwise stated, refer to the behavior of *one grain* of the solution.

1. *Ammonia.*

Aqua ammoniæ produces in solutions of corrosive sublimate a white, flocculent precipitate known as *mercurammonium chloride*, $HgNH_2Cl$; thus: $HgCl_2 + 2NH_4HO = HgNH_2Cl + NH_4Cl + 2H_2O$. The precipitate is soluble in large excess of the precipitant, and readily soluble in the mineral acids; it is also soluble in some of the salts of ammonium, but insoluble in ammonium chloride.

1. $\frac{1}{100}$ grain of corrosive sublimate, in one grain of water, yields with the reagent a very abundant precipitate. If the mercurial solution be exposed to the *vapor* of ammonia, it yields the same reaction.
2. $\frac{1}{1000}$ grain yields a quite good deposit.
3. $\frac{1}{5000}$ grain: a quite satisfactory reaction by either ammonia or its vapor.
4. $\frac{1}{10,000}$ grain: a quite perceptible turbidity.

This reagent also produces white precipitates in solutions of various other substances besides mercuric combinations. But if the mercurial precipitate be dried and heated, it readily volatilizes without residue, in which respect it differs from all other metallic precipitates produced by the reagent. When heated with a solution of potassium hydrate, the precipitate is decomposed, with the production

of yellow oxide of mercury. The precipitate is also decomposed by stannous chloride, with the separation of metallic mercury.

2. *Potassium and Sodium Hydrates.*

The fixed caustic alkalies, when added in not sufficient quantity to effect complete decomposition, throw down from quite strong solutions of corrosive sublimate *reddish-brown* amorphous precipitates consisting of a compound of mercuric oxide and the undecomposed chloride of the metal; but when the reagent is added in excess the precipitate has a *yellow* color, and consists alone of mercuric oxide, HgO. The precipitate is insoluble in excess of the precipitant, but readily soluble in free acids.

1. $\frac{1}{100}$ grain of corrosive sublimate yields a rather copious, reddish-brown or yellow deposit.
2. $\frac{1}{500}$ grain yields only a slight cloudiness.

The production of a reddish-brown precipitate, which becomes yellow upon the further addition of the alkaline reagent, is peculiar to mercuric combinations. The only other metals that yield *yellow* precipitates with the reagent are the rare substances platinum and uranium: the precipitate from the former of these is usually in the form of octahedral crystals; but the precipitate from the latter, like that from mercurial compounds, is amorphous and insoluble in excess of the precipitant.

When the precipitated mercuric oxide is collected, dried, and strongly heated in a reduction-tube, it undergoes decomposition, with the evolution of free oxygen gas and the production of a globular sublimate of metallic mercury. This reaction will serve for the identification of the merest trace of the mercurial precipitate. The presence of the chlorine of the corrosive sublimate in the liquid from which the mercury was precipitated may be shown by acidulating the solution with nitric acid, and then adding silver nitrate, when it will yield a white precipitate of silver chloride.

The *normal carbonates of the fixed alkalies*, when added in limited quantity, throw down from one grain of a 1–100th solution of corrosive sublimate a quite good yellowish precipitate; when an excess of the reagent is employed, the precipitate has a brick-red color. A similar quantity of a 1–500th solution of the salt yields only a slight turbidity.

3. *Potassium Iodide.*

This reagent produces in solutions of corrosive sublimate a bright scarlet amorphous precipitate of mercuric iodide, HgI_2, which is readily soluble in excess of the precipitant, as well as in large excess of the mercurial solution. At first the precipitate has frequently a yellow color, but it quickly becomes scarlet, except if only in minute quantity, when the yellow color may be permanent. The iodide of mercury is also soluble in the alkaline chlorides and in alcohol, but only slowly soluble in the diluted mineral acids; strong nitric and sulphuric acids readily decompose it, with the elimination of iodine.

1. $\frac{1}{100}$ grain of the salt yields a copious, scarlet precipitate.
2. $\frac{1}{1000}$ grain: a reddish-yellow deposit.
3. $\frac{1}{2500}$ grain yields, with a very minute quantity of the reagent, a quite satisfactory yellow precipitate.

The production of a scarlet precipitate by this reagent is peculiar to solutions of mercuric salts. The iodide of mercury, when washed, dried, and heated in a reduction-tube, volatilizes unchanged, and recondenses in the form of a yellow, partly crystalline sublimate, the color of which slowly changes to scarlet. When the dried precipitate is intimately mixed with recently ignited sodium carbonate and heated in a reduction-tube, it yields a sublimate of metallic mercury.

4. *Sulphuretted Hydrogen.*

When somewhat concentrated neutral or acidulated solutions of corrosive sublimate are treated with a relatively small quantity of sulphuretted hydrogen gas or of ammonium sulphide, they yield a precipitate which, at least when the mixture is agitated, has a pure *white* color, and consists of mercuric sulphide and undecomposed corrosive sublimate. On the further addition of the reagent, the precipitate acquires a yellow, then a brown color, and finally becomes *black*, when it consists alone of the sulphide of mercury. From more dilute solutions the precipitate has at first a brownish color.

The precipitated mercuric sulphide is insoluble in nitric and hydrochloric acids, even on the application of heat; but it is readily decomposed and dissolved by cold nitro-hydrochloric acid, with the separation of free sulphur and the formation of mercuric chloride

and more or less mercuric sulphate, the latter compound being derived from the oxidation of some of the sulphur. It is insoluble in the caustic alkalies, and in the alkaline sulphides.

The following results in regard to the reactions of this test refer to the behavior of *ten grains* of the corrosive sublimate solution when acidulated with hydrochloric acid and subjected to the action of a slow stream of the washed sulphuretted gas.

1. 1–100th solution ($=\frac{1}{10}$ grain of $HgCl_2$) yields an immediate brownish precipitate, which soon assumes a dark brown color, and ultimately becomes black, the final precipitate being quite copious.
2. 1–1000th solution yields a yellowish-brown, brown, then a rather copious black precipitate.
3. 1–10,000th solution: the liquid immediately assumes a brownish color, then small brownish flakes separate, and after a little time there is a good brownish deposit.
4. 1–25,000th solution: almost immediately the liquid assumes a yellowish color, and in a few minutes very small brownish flakes appear, which after some time subside to a very distinct deposit.
5. 1–50,000th solution: very soon the fluid becomes turbid, and after standing some time throws down a just perceptible yellowish precipitate.
6. 1–100,000th solution, when saturated with the gas and allowed to stand several hours, undergoes no well-marked change.

The progressive change of color from white to black, of the precipitate produced by this reagent, is peculiar to solutions of mercuric salts. But this change, as shown above, is well marked only in comparatively strong solutions of the mercurial salt; and the production of a black or brownish precipitate is not in itself characteristic of mercury, since there are several other metals that yield similar results, even from acidulated solutions.

Mercuric sulphide differs from all other black precipitates, produced under like conditions, in that when thoroughly dried, and heated in a reduction-tube, it completely volatilizes, without residue or decomposition, and yields a black sublimate having a metallic appearance. Again, when mixed with anhydrous sodium carbonate, and heated in a reduction-tube, it undergoes decomposition, with the production of a globular sublimate of metallic mercury. Either of

these methods (but the latter is preferable) will serve for the identification of very minute traces of the mercurial compound.

If the liquid from which the mercury was precipitated by the sulphur reagent was not acidulated with hydrochloric acid previous to the application of the reagent, it will serve for the detection of the chlorine of the corrosive sublimate, which element now exists as free hydrochloric acid. For this purpose the filtered liquid is gently heated until the odor of the sulphuretted hydrogen has entirely disappeared, and then treated with a solution of silver nitrate.

5. *Stannous Chloride.*

When a *limited* quantity of stannous chloride is added to solutions of corrosive sublimate, the latter, giving up a portion of its chlorine to the tin, is reduced to mercurious chloride, or calomel, which falls as a white precipitate, the reaction being $2HgCl_2 + SnCl_2 = SnCl_4 + Hg_2Cl_2$. In the presence of an *excess* of the reagent the mercury is entirely deprived of its chlorine, and separates as a dark gray precipitate of exceedingly minute globules of the metal. The reaction in this case is $HgCl_2 + SnCl_2 = SnCl_4 + Hg$. The separation and subsidence of the metallic precipitate are much facilitated by heating the mixture with a little hydrochloric acid; if the clear supernatant liquid be then decanted, and the residue again heated with a little fresh hydrochloric acid, the finely divided mercury will unite into larger globules. The hydrochloric acid employed in this operation should be perfectly free from nitric acid, otherwise the metallic globules may disappear, being dissolved. This test may be conveniently applied in a watch-glass.

1. $\frac{1}{100}$ grain of corrosive sublimate, in one grain of water, yields with the reagent a rather copious precipitate, which at first is white, but quickly changes to a gray color, and then becomes almost black.
2. $\frac{1}{1000}$ grain yields much the same results as 1.
3. $\frac{1}{5000}$ grain: a quite good precipitate.
4. $\frac{1}{10,000}$ grain yields a quite distinct reaction.

The production of metallic globules by this test is, of course, peculiar to solutions of mercury. When the precipitate is present in only minute quantity, its globular nature may still be readily recognized by means of a hand-lens or a low power of the microscope. If the precipitate be stirred with a small piece of bright

copper-foil, the latter receives a coating of metallic mercury, which when rubbed by a soft body assumes a bright silvery appearance. In this manner, especially by the aid of a drop of hydrochloric acid and a gentle heat, the true nature of a mercurial deposit that will not furnish satisfactory globules may sometimes be readily determined.

It is important to bear in mind, in the application of this test, that the reaction of stannous chloride is interfered with or entirely prevented by the presence of alkaline chlorates, and also of free nitric acid.

6. *Copper Test.*

When a small slip of bright copper-foil is placed in a normal solution of corrosive sublimate, the latter is decomposed, with the deposition of metallic mercury upon the copper. The delicacy of this reaction is much increased by acidulating the solution with hydrochloric acid, and also by heat. The deposited mercury, when separated from normal solutions of the salt, has usually a dark gray color; whilst when from acidulated solutions it has generally a bright silvery appearance: its exact appearance, however, will depend much upon the thickness of the deposit, which in its turn will, of course, depend upon the strength of the solution and the size of the copper-foil employed. When the deposit has a dull color, it immediately acquires a bright, mirror-like appearance on being rubbed with a piece of soft wood or any similar substance.

The same metallic deposit will, of course, make its appearance when a drop of the mercury solution is placed on a piece of bright copper plate. Under these circumstances, it has been proposed to touch the copper, through the mercurial solution, with a needle of zinc. This somewhat facilitates the decomposition of the mercurial compound, but at the same time it causes the separated mercury to be distributed over a greater surface, part of it being deposited upon the immersed end of the zinc.

When a small piece of the coated copper-foil is carefully washed, dried at a moderate temperature, in a water-bath, and heated in a narrow, perfectly dry reduction-tube, the mercury volatilizes, and recondenses in the cooler portion of the tube, forming a mist-like sublimate. Under a low power of the microscope, this sublimate will be found to consist of innumerable spherical globules, which are opaque to transmitted light and present a bright silvery appearance

when viewed under incident light. These characters readily distinguish the mercurial from all other sublimates.

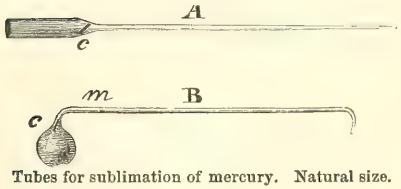
In the following investigations in regard to the limit of this test, *one grain* of the mercurial solution, placed in a thin watch-glass, was acidulated with hydrochloric acid, and the mixture heated with a small fragment of the copper-foil.

1. $\frac{1}{100}$ grain of corrosive sublimate imparts to the copper an immediate lustre, and very soon the deposit becomes comparatively thick. This reaction takes place about equally well without the presence of the free acid or the aid of heat. The copper employed should measure about $\frac{1}{5}$ by $\frac{1}{10}$ of an inch in extent. When the washed and dried coated copper is heated in a narrow reduction-tube, it yields a very good globular sublimate, many of the globules measuring $\frac{1}{100}$ of an inch in diameter.
2. $\frac{1}{1000}$ grain: when the copper employed measures about $\frac{1}{8}$ by $\frac{1}{12}$ of an inch in extent, it immediately assumes a silvery appearance, and in a little time receives a gray coating. Similar results are obtained without the aid of heat. Without either the free acid or heat, the deposit begins to form in a very little time; by heat alone, immediately. The coated copper, when heated in a small reduction-tube, yields a very satisfactory globular sublimate.
3. $\frac{1}{10,000}$ grain: when the acidulated liquid is heated with a slip of copper measuring about $\frac{1}{10}$ by $\frac{1}{20}$ of an inch in extent, the mercurial deposit manifests itself immediately, and very soon becomes satisfactory. If the coated copper be heated in a very narrow reduction-tube, it yields a sublimate which is quite perceptible to the naked eye, and which, under the microscope, is found to consist of innumerable spherical globules.

When deposits but little smaller than that just considered are heated in a reduction-tube of the ordinary form, even of very narrow bore, the results are by no means uniform. Very uniform results, however, may be obtained in the following manner. A quite thin and perfectly clean tube, of about 1–10th of an inch in diameter, is drawn out into a small capillary neck, as shown in Fig. 11, A. The coated copper is then introduced, through the wider portion of the cooled tube, to the point *c*, the neck of the tube moistened with water or wrapped with wet cotton, and the wider end very carefully fused shut by a small blow-pipe flame, when the fusion is slowly advanced to

the copper, as illustrated in B. The capillary end of the tube may now be fused shut. When the tube, thus prepared, is wiped and examined under the microscope, the mercurial sublimate will be found at about the point *m*, forming a narrow ring of well-defined globules. This method also possesses the advantage of allowing the higher powers of the microscope to be applied, since these tubes may readily be prepared with walls not exceeding 1–200th of an inch in thickness. The tube containing the sublimate may be reserved for future reference: after long periods, however, the sublimate deteriorates somewhat, and may even, if only in minute quantity, entirely disappear.

FIG. 11.



Tubes for sublimation of mercury. Natural size.

4. $\frac{1}{25,000}$ grain: if the acidulated solution be heated, and as the liquid evaporates its place supplied with pure water, the copper in a little time presents a silvery appearance, and before long acquires a very decided gray coating. When the coated copper is heated in a tube of the above form, it yields a sublimate which is visible to the unaided eye, and which, under an amplification of about seventy-five diameters, is found to consist of a ring of well-defined globules. In a number of instances over one hundred globules, varying in size from 1–1000th to 1–10,000th of an inch in diameter, were counted in a single field of the objective; many of the globules measured over 1–2333d of an inch in diameter.
5. $\frac{1}{50,000}$ grain: when the slip of copper employed measures only about $\frac{1}{20}$ by $\frac{1}{40}$ of an inch in extent, the results obtained are very similar to those described under 4.
6. $\frac{1}{100,000}$ grain: the copper, after continued heating and renewal of the evaporated liquid by water, acquires a quite distinct metallic tarnish, and when heated in a tube of the above form, yields a very satisfactory globular sublimate. In some few instances over one hundred globules were obtained, several of which, singly, measured over 1–1750th of an inch in diameter; the greater number of the globules, however, were quite small: none less than the 1–10,000th of an inch in diameter were counted. In a majority of the experiments made, the sublimate

contained about fifty well-defined globules, most of which were usually in a single field of a two-thirds inch object-glass. So far as the evidence of the presence of mercury is concerned, this quantity of corrosive sublimate, when manipulated in the above manner, will yield just as satisfactory results as a much larger quantity, the only difference being in the absolute number and size of the globules obtained.

7. $\frac{1}{500,000}$ grain: the copper, even after prolonged heating, undergoes but little change in appearance. But when washed, dried, and heated in a tube, as many as twenty satisfactory mercurial globules were obtained, the largest of which measured about 1–3000th of an inch in diameter; the diameter of most of them, however, varied from 1–5000th to 1–10,000th of an inch. Most of the sublimates obtained contained from five to ten globules measuring or exceeding 1–5000th of an inch in diameter.

For the identification of these mercurial globules an amplification of about seventy-five diameters is generally the most useful. Under this power a globule measuring 1–3000th of an inch in diameter is very readily identified: such a globule, if a perfect sphere, would weigh only about the 1–15,000,000th of a grain. So, also, under this power, globules of the 1–5000th of an inch in diameter are very distinct and quite satisfactory: a globule of this size would weigh about 1–70,000,000th of a grain. And even when of 1–7000th of an inch, their spherical nature may still be determined with considerable certainty: such a globule would weigh only about 1–190,000,000th of a grain. But under this amplification globules of only 1–10,000th of an inch in diameter appear as mere opaque points under transmitted light. Under an amplification of about two hundred and fifty, a globule of 1–10,000th of an inch in diameter may be satisfactorily determined; and even when of only the 1–15,000th of an inch, their spherical outline may still be recognized with considerable certainty.

On account of the curvature of the glass tube, a one-fifth inch objective, or an amplification of about two hundred and fifty diameters, is about the highest power that can be satisfactorily employed for these identifications. When upon a *flat* surface, the true nature of globules much smaller than any of those mentioned above can be readily determined. Thus, with a one-eighth inch objective a

globule, or "artificial star," measuring only the 1–25,000th of an inch in diameter, and weighing about 1–9,000,000,000th of a grain, will present the characters of sphericity and opacity, and reflect incident light. It need hardly be observed that it is not intended to imply that quantities of mercury in themselves no greater than these can be recovered from a solution and reproduced in the globular form. From the above experiments it would appear that even under the most favorable conditions the least quantity of corrosive sublimate from which the mercury can thus be reproduced is about the 1–100,000th, or at least 1–500,000th, of a grain.

It may be remarked that in the above experiments the amount of metallic mercury present in the corrosive sublimate was as 100 is to 135.5. It may also be added that from these experiments it would appear that mercury is not as readily volatilized by continued heating with boiling water as is usually supposed. This view is also borne out by the experiments of Fresenius. (*Quantitative Analysis.*)

The test now under consideration has an advantage over ordinary liquid tests, in that it is not as readily affected by dilution. Thus, ten grains of a 1–100,000th solution of the mercurial compound will yield after a time, even upon renewal of the evaporated liquid, very nearly as good results as one grain of a 1–10,000th solution. Beyond a certain limit, however, this, like all other tests, will entirely fail to act. Another advantage possessed by this test is that while being applied to a solution the latter may be concentrated to almost any extent.

Fallacies.—The mere fact of a metallic deposit being formed upon the copper, in the application of this test, is not in itself positive evidence of the presence of mercury, especially if the solution be acidulated and heated, since arsenic, antimony, silver, bismuth, platinum, palladium, and some few other metals are deposited under similar conditions. Of these various metals, however, the only ones that, like mercury, have a white silvery appearance are silver and bismuth. Moreover, the only ones which, like that metal, will deposit from *cold* solutions are silver, platinum, and palladium. When, therefore, the deposition takes place from a cold solution, and has a bright silvery lustre, or acquires it by friction, the deposit is most probably mercury; but it might be silver.

Of the various metals that might thus be deposited, even from heated acidulated solutions, the only ones that will volatilize and

yield a sublimate, when the coated copper is heated in a reduction-tube, are mercury, arsenic, and antimony. But the spherical nature, as well as the opacity, of the globules under transmitted light, and their bright silvery lustre under incident light, of the mercurial sublimate, readily distinguish it from the octahedral crystalline sublimate produced by arsenic, and from the deposit occasioned by antimony.

Metallic zinc, bismuth, cadmium, tin, silver, nickel, iron, lead, arsenic, and antimony will also, like copper, decompose solutions of corrosive sublimate, with the formation of a coating of metallic mercury upon the applied metal. But neither of these metals has for this purpose any advantage over metallic copper, and in most instances the reaction is very much less delicate than when that metal is employed.

So, also, if the acidulated mercurial solution be placed in a small platinum or gold dish and the metal touched, through the solution, with a thin wire of zinc, iron, tin, or any other of the above-named metals, the salt undergoes decomposition by galvanic action, the mercury being deposited chiefly upon the platinum or gold, but partly upon the other metal. Similar results may be obtained by applying a small slip of gold or platinum-foil to a corresponding slip of tin, zinc, or iron, or to a small cylinder of either of these metals, and immersing the combination in the acidulated mercurial solution. Some of these galvanic combinations are extremely delicate in their reactions; but they are not as well adapted for the detection of very minute quantities of mercury as the method by copper alone, as before described.

7. *Silver Nitrate.*

This reagent decomposes neutral and acidulated solutions of corrosive sublimate, with the production of a white, amorphous precipitate of silver chloride, AgCl, which is insoluble in nitric acid. In its pure state silver chloride is very readily soluble in ammonia, but as precipitated from the mercurial solution, which itself yields a precipitate with ammonia, it is soluble with difficulty in that alkali, and, unless very large excess of the alkali be added, is soon replaced by a white, granular deposit.

1. $\frac{1}{100}$ grain of corrosive sublimate, in one grain of water, yields a very copious, white, curdy precipitate.

2. $\frac{1}{1000}$ grain yields a quite good precipitate, which, in the mixture, dissolves with difficulty in ammonia.
3. $\frac{1}{10,000}$ grain: a good deposit, which quickly disappears on the addition of ammonia.
4. $\frac{1}{50,000}$ grain yields a quite fair precipitate.
5. $\frac{1}{100,000}$ grain: a very satisfactory turbidity.
6. $\frac{1}{500,000}$ grain yields a perceptible cloudiness.

This reagent is simply for the purpose of detecting the presence of the *chlorine* of the corrosive sublimate. The reaction of the reagent is, of course, common to solutions of all soluble chlorides and of free hydrochloric acid. If, however, it be shown by any of the other tests that the solution also contains mercury, then it follows, providing the solution is not a complex mixture, that the metal existed as corrosive sublimate, since this is its only soluble chloride.

Other Reagents.—The mercury from solutions of corrosive sublimate may be precipitated, in a state of combination, by several reagents other than those already described, but the reactions of these are much less delicate and characteristic than those already considered. A few of these tests, however, may be very briefly mentioned.

Potassium ferrocyanide produces in solutions of the mercurial compound a dirty-white precipitate, which is soluble in excess of the precipitant. One grain of a 1–100th solution of the salt yields a very copious precipitate; and a similar quantity of a 1–1000th solution, a quite good deposit. This is about the limit of the reaction of the test for one grain of the solution.

Potassium ferricyanide throws down from aqueous solutions of the salt a greenish-yellow, amorphous precipitate, which is insoluble in excess of the precipitant. One grain of a 1–1000th solution of the mercurial compound yields a quite good precipitate; a similar quantity of a 1–5000th solution yields only a slight turbidity.

Potassium chromate produces in quite strong solutions of the salt a greenish-yellow precipitate; but the *dichromate* occasions no visible reaction.

Separation from Organic Mixtures.

Since corrosive sublimate is readily precipitated, with more or less decomposition, by various animal and vegetable principles, much of the poison, when added to mixtures of this kind, may be present in a form insoluble in water. Under these circumstances, however,

sufficient of the mercury to be detected by the ordinary reagents will usually remain in solution, even in quite complex mixtures, and after standing for long periods. We find that the solid coagulum resulting from the precipitation of the poison with albumen, which is one of the most insoluble compounds of this kind, when washed and dried, even to a horny mass, still yields up some of the mercurial compound on digestion with even cold water; more of it to hot water; and still more when boiled with water acidulated with hydrochloric acid.

Suspected Solutions.—Any precipitate or mechanically suspended matter present is separated from the suspected solution by a filter, and examined for any solid particles of the poison, then washed with warm water, and reserved for future examination, if necessary. A portion of the clear liquid may then be acidulated with hydrochloric acid and boiled with a small slip of bright copper-foil. If the copper quickly receives a metallic coating, it is removed from the liquid, and other and larger slips of the metal consecutively added, as long as they acquire a deposit. If the deposit thus obtained consists of mercury, it will usually present a grayish-white appearance, and acquire a bright silvery lustre when gently rubbed with the finger or any other soft body. The coated copper is then washed in alcohol or ether, dried at a moderate temperature, one or more of the slips heated in an appropriate reduction-tube, and any sublimate obtained examined by a low power of the microscope.

If the method now described yields positive results, these may be confirmed by examining other portions of the suspected liquid by some of the other tests for the poison; this, however, is not really necessary, at least so far as the presence of mercury is concerned. A portion of the liquid should be concentrated to a small volume, and allowed to stand in a cool place for some hours, or longer if necessary, in order that the poison, if present, may separate in its crystalline state. Any crystals thus obtained, after being carefully washed, are dissolved in a small quantity of water, and a portion of the solution tested for chlorine by silver nitrate.

Should the copper test, after prolonged heating and concentration of the liquid, fail to reveal the presence of mercury, it is quite certain that the other tests for this metal would also fail, since they are much less delicate in their reaction than the former. Under these circumstances, any organic solids separated from the suspected liquid, by

filtration, are boiled for about ten minutes with pure water, or, better still, so far as the recovery of mercury is concerned, with water strongly acidulated with hydrochloric acid; the cooled liquid is then filtered, and the filtrate examined by the copper test, in the manner above described. It is obvious that the employment of hydrochloric acid in the preparation of the liquid will, in the event of the detection of mercury, preclude the possibility of proving that the metal existed as a chloride, at least so far as the liquid under examination is concerned.

Another method for the recovery of corrosive sublimate from organic liquids is to agitate violently the concentrated liquid, for some minutes, in a small bottle or a stout test-tube, with about twice its volume of pure commercial ether, in which, as we have already seen, the salt is freely soluble. When the liquids have completely separated, which will usually require a repose of only a few minutes, the ethereal fluid is carefully decanted into a watch-glass, and allowed to evaporate spontaneously. Any saline residue thus obtained is examined in the usual manner, a portion of it being first examined by some of the tests for the poison in its solid state. In the application of this method it should be borne in mind that ether does not extract the whole of the salt from its aqueous solutions.

Vomited matters.—The matters ejected from the stomach may be examined in the same manner as just described for suspected solutions. If an antidote, such as white of egg or gluten, was administered, the organic solids of the vomited matters may require long boiling with water strongly acidulated with hydrochloric acid, for the complete separation of the poison.

Contents of the Stomach.—As corrosive sublimate is readily soluble, it is not often found in its solid state in the stomach: however, this examination should not be omitted. The mass is then stirred with sufficient water to make it quite liquid, the mixture gently heated for some time on a water-bath, the cooled liquid filtered, and the solids on the filter well washed with pure water, the washings being collected with the first filtrate. The filter, with its contents, should be reserved. The clear liquid is then concentrated to an appropriate volume, and, if necessary, again filtered.

A portion of the filtrate thus obtained is acidulated with hydrochloric acid, and boiled with a very small slip of bright copper-foil. If this fails to receive a metallic coating, the application of the

heat should be continued until the liquid is evaporated to near dryness, before concluding that the poison is entirely absent. On the other hand, if the copper quickly receives a metallic deposit, it is removed from the liquid, and other slips of the metal added as long as they become coated. The mercurial deposit, as already pointed out, is readily distinguished from that produced by arsenic, antimony, and most other metals that are thus deposited, by its bright silvery appearance, at least when rubbed. The coated copper is thoroughly washed in alcohol or ether, dried, then heated in a reduction-tube, and any sublimate thus obtained examined by the microscope.

Another portion of the filtrate may be acidulated with hydrochloric acid, and treated with excess of a solution of stannous chloride, when, if it yields a dark gray precipitate, the mixture is gently heated until the precipitate has completely subsided; the supernatant fluid is then decanted, the residue washed with hot water, then boiled with a little water strongly acidulated with pure hydrochloric acid, which will cause any finely divided mercury present to collect into comparatively large globules. It must be remembered that various organic solutions yield with the tin reagent a white precipitate, which may more or less conceal the color of the mercurial deposit. Under these circumstances, the precipitate is boiled for some time with a strong solution of caustic potash, which will dissolve the organic matter, leaving the mercury in the form of a grayish-black powder. This is then boiled with a little diluted hydrochloric acid, in the manner just described.

If a portion of the filtrate be acidulated with hydrochloric acid and treated with sulphuretted hydrogen gas, any of the poison present will give rise to sulphide of mercury, which will be thrown down as a black precipitate, at least if excess of the reagent has been employed. After the precipitate has completely subsided, it may be collected on a filter, washed, and then dried. Its mercurial nature may be established by mixing it with several times its volume of recently ignited sodium carbonate and heating the mixture in a reduction-tube, when it will undergo decomposition with the production of a globular sublimate of metallic mercury, readily identified by means of the microscope.

The positive reaction of either of the foregoing tests would, of course, simply indicate the presence of the mercury of the corrosive sublimate. For the purpose of showing the presence of the *chlorine*,

it is best to agitate a portion of the filtrate with ether, in the manner already directed, then allow the ethereal solution to evaporate spontaneously, dissolve the residue in a small quantity of warm water, and treat the solution with silver nitrate. As the alkaline chlorides are *insoluble* in ether, the detection of chlorine under these circumstances would not be open to the objection that would hold if the silver reagent were applied directly to the original filtrate: especially will this objection be guarded against if the ethereal liquid, on evaporation, leave the poison in its crystalline state.

Should the methods already given fail to reveal the presence of mercury in the filtrate, then the organic solids left upon the filter may be examined. For this purpose the mass is transferred to a porcelain dish, the solids cut into small pieces, and boiled for about twenty minutes with pure water, the mixture being frequently stirred by means of a glass rod. When the mixture has cooled, the liquid portion is separated by a filter, the filtrate concentrated to a small volume, and then examined in the manner before directed for the first filtrate. Instead of boiling the organic solids with pure water, they may be boiled with water containing hydrochloric acid until they are entirely disintegrated. If, however, this method be employed, the presence of the chlorine of the corrosive sublimate cannot be established.

Another method for the examination of the above organic solids is to boil the mass with a somewhat concentrated solution of potassium hydrate until the solids are entirely decomposed, and then treat the mixture with a solution of stannous chloride, the heat being continued for some little time after the addition of the tin reagent. Any dark gray precipitate thus obtained is carefully collected, washed, and examined in the manner already described.

From the Tissues.—If there has been a failure to detect corrosive sublimate under one or other of the conditions now described, it will no longer be possible to show the presence of the poison as a whole; but the presence of the absorbed mercury may be shown in some of the soft tissues of the body. For the recovery of the absorbed metal various methods have been advised. The finely divided tissue, as about ten ounces of the liver, may be made into a thin paste with water containing about one-sixth of its volume of pure hydrochloric acid, and the whole heated at about the boiling temperature until the organic solids are completely disintegrated, which

will usually require about two hours. The mass is then allowed to cool, transferred to a linen strainer, the strained liquid filtered, and then concentrated to a comparatively small volume. A portion of the liquid may now be heated to the boiling temperature, and examined by the copper test, employing at first only a very minute slip of the metal. In applying this test, it should be remembered that the copper, after prolonged heating, may acquire a very distinct stain or tarnish, even in the absence of mercury or of any other metal. Before heating the copper in a reduction-tube it should be very thoroughly washed, first in water containing a little ammonia. Should the first portion of liquid examined fail to reveal the presence of mercury, then another and larger portion, or even the whole of the remaining liquid, should be examined in a similar manner.

The copper test will serve to recover very minute quantities of mercury from very complex organic liquids. A portion of a human liver, free from mercury, was boiled with diluted hydrochloric acid in the manner just described, and the liquid strained. To one hundred grain-measures of the strained fluid the 1–1000th of a grain of corrosive sublimate was added,—the poison then being under a dilution of 100,000 times its weight of the organic liquid,—and the mixture boiled with a very small slip of bright copper-foil. After a little time the copper received a very distinct metallic stain, and, when washed, dried, and heated in a small reduction-tube, yielded a sublimate which, under the microscope, was found to contain over one hundred characteristic globules of mercury.

Should the examination of the first portion of the above liquid indicate the presence of mercury, and it be desired to pursue the investigation, another portion may be treated with excess of stannous chloride, and gently warmed, until the precipitate has completely deposited. The precipitate is then collected, washed, and boiled in a porcelain evaporating-dish with a solution of potassium hydrate until the organic matter is dissolved and the residue assumes a dark gray color. The clear supernatant liquid is then decanted, and the residue repeatedly washed with hot water, then boiled with hydrochloric acid, which will cause any finely divided mercury present, if entirely free from foreign matter, to coalesce into globules.

Another, and in some cases preferable, method for breaking up the animal tissues is by means of hydrochloric acid and potassium chlorate, in the manner described for the recovery of absorbed arsenic.

The finely divided tissue is treated with about one-fourth of its weight of pure concentrated hydrochloric acid, and the whole made into a thin paste by the addition of water. The mixture is then heated to about the boiling temperature, and small quantities of powdered potassium chlorate occasionally added until the mass becomes perfectly homogeneous, after which it is kept at a gentle heat until the odor of chlorine has entirely disappeared. The mixture is now allowed to cool, the liquid filtered, and the solid matters on the filter well washed with hot water. The filtrate may now be *partially* neutralized with pure sodium carbonate, and concentrated until its volume is about three times that of the hydrochloric acid employed in the destruction of the organic matter.

The liquid thus obtained, after filtration if necessary, is exposed for several hours to a slow stream of sulphuretted hydrogen gas, then gently heated, and allowed to stand in a moderately warm place for about fifteen hours. Any mercury present will now be in the precipitate, in the form of the black sulphide, together with more or less organic matter, the color of which may disguise that of the mercurial compound. The precipitate is collected upon a small filter, well washed, and then transferred to a porcelain dish, treated with a proportionate quantity of concentrated hydrochloric acid, and pure nitric acid added drop by drop until complete solution has taken place. By this treatment with the mixed acids the mercury of the mercurial sulphide will be dissolved to mercuric chloride, while the sulphur will be eliminated as a yellow adherent mass, which as it forms should be removed by means of a glass rod. On now cautiously evaporating the solution to dryness on a water-bath, the mercuric chloride will be left as a white crystalline mass; if the eliminated sulphur was not removed from the mixture, the residue may consist largely of mercuric sulphate.

A portion of the saline residue thus obtained may be tested for the poison in its solid state, and another portion dissolved in a small quantity of water, and the solution examined by the copper test. If the addition of water produces an insoluble yellow sulphate of mercury, its solution may be readily effected by the addition of a drop or two of hydrochloric acid.

From the Urine.—About 300 c.c., or twelve fluid ounces, of the urine are strongly acidulated with hydrochloric acid, evaporated to a small volume, filtered, the filtrate boiled with a small slip of bright

copper-foil, and the latter washed, dried, and examined in the usual manner. Another method for the examination of this fluid is to concentrate it to near dryness, and then destroy the organic matter by means of hydrochloric acid and potassium chlorate, in the manner described for the recovery of the poison from the tissues. If the first of these methods be adopted and there is a failure to detect the metal, any solids separated by filtration should be examined.

Dr. Thudichum remarks (*Pathology of the Urine*, 408) that in all cases where the urine contains mercury there is at the same time a peculiar albuminous substance present in it, which with nitric acid yields a faint reaction of albumen. A substance is also present having the reactions of sugar. In some cases of mercurialism, he adds, the metal only appeared in the urine at intervals, even where the symptoms had undergone no remission.

Failure to detect the Poison.—It has not unfrequently happened in acute corrosive sublimate poisoning that there was a failure to detect the poison in any part of the dead body. In a case quoted by Dr. Beck (*Med. Jur.*, ii. 638), in which a woman had poisoned herself with this substance, not a trace of the poison was found either in the matters vomited during life or in the contents of the stomach after death. So, also, in a case cited by Wharton and Stillé (*Med. Jur.*, 538), none of the poison was detected in the stomach and intestines of a young man who had taken three drachms of corrosive sublimate, and died from its effects on the sixth day. In another instance, recorded by Dr. Taylor (*On Poisons*, 471), in which two drachms were swallowed, and death occurred on the fourth day, a chemical examination of the stomach, blood, and tissues failed to reveal the presence of mercury.

According to the observations of I. L. Orfila, absorbed mercury is eliminated from the system chiefly by means of the kidneys. In examining the urine of patients treated with mercurial preparations, he found the metal five days after it had ceased to be taken, but in eight days it was no longer discovered. In experiments upon dogs, he found the metal in the tissue of the stomach and liver of some of the animals as late as the eighteenth day, but in others, similarly treated, it had entirely disappeared. (*Orfila's Toxicologie*, 1852, i. 680.)

When mercury remains in the body at the time of death, it, like

arsenic, may be recovered after very long periods. In a case of corrosive sublimate poisoning, which we examined some years since, and in which death occurred on the fourth day, the metal was readily detected in the *stomach* and *liver* of the body after it had been buried *nine months:* none of the other organs were chemically examined. It need hardly be remarked that, since mercurial preparations are so frequently taken medicinally, the detection of minute traces of the metal in the dead body would not in itself be any evidence that it was the cause of death.

According to the researches of J. G. Smith, Ph.G. (*Amer. Jour. Pharm.*, Aug. 1877, 397), commercial corrosive sublimate is frequently contaminated with minute quantities of arsenic, most likely derived from the sulphuric acid used in preparing the mercuric sulphate, from which afterward the mercuric chloride is sublimed. In five samples of the salt in which the arsenic was determined quantitatively, the proportion of this metal, expressed as arsenic oxide, varied from 0.033 to 0.096 per cent.

Quantitative Analysis.—The quantity of corrosive sublimate present in a solution of the salt may be readily estimated by precipitating the metal as mercuric sulphide. For this purpose, the solution, acidulated with hydrochloric acid, is saturated with a slow stream of washed sulphuretted hydrogen gas, after which it is allowed to stand in a moderately warm place until the precipitate has completely subsided; the precipitate is then collected on a small filter of known weight, washed with pure water until the washings no longer have an acid reaction, dried on a water-bath at 100° C. (212° F.), and weighed. One hundred parts by weight of the dried sulphide correspond to 116.81 parts of anhydrous corrosive sublimate, or 86.20 parts of metallic mercury.

If in the application of the tin test a known quantity of the mercurial solution was employed, any globules of metallic mercury obtained may be carefully washed, dried, and weighed. One hundred parts by weight of the pure metal represent 135.5 parts of corrosive sublimate.

CHAPTER VII.

LEAD, COPPER, ZINC.

Section 1.—Lead.

History and Chemical Nature.—Lead is one of the elementary metals. Its symbol is Pb; its atomic weight 207; and its density 11.44. It is found in nature associated with several other elements, but it occurs principally as sulphide of lead, or galena. Lead has a bluish-gray color and a strong metallic lustre; it is quite soft, being easily scratched by the finger-nail, and leaves a well-known mark upon white paper. It is very malleable, and fuses at about 315.5° C. (600° F.).

In its pure state lead is unacted upon by *pure* water. But if air be present in the liquid, or its surface be freely exposed to the action of the atmosphere, the metal rapidly becomes corroded, and gives rise to oxide of lead, which partly unites with water and partly with carbonic acid, forming a hydrated oxycarbonate of lead. This compound partly deposits upon the lead as silky scales or falls as a precipitate, while a portion remains mechanically suspended in the liquid; at the same time some little of the compound becomes dissolved. When, however, the water holds in solution certain salts, such as the carbonates, sulphates, or phosphates, an insoluble crust of lead salt slowly deposits upon the metal and protects it from further action, and thus none of the lead is dissolved. On the other hand, the presence of chlorides and of nitrates increases the corrosive action of water. Dr. Frankland found that water which acted on lead lost this power after passing through a filter of animal charcoal, owing to a minute quantity of calcium phosphate passing into the water from the charcoal. (*Chem. News*, Dec. 1868, 296.)

Lead is readily soluble in diluted nitric acid, especially upon the application of heat, with the formation of lead nitrate, and the

evolution of nitrous fumes. Cold diluted sulphuric acid fails to dissolve it, but the hot concentrated acid dissolves it to lead sulphate, with the evolution of sulphurous oxide gas. Hydrochloric acid, even under the application of heat, has but little action upon the metal. Heated on charcoal before the blow-pipe flame, it gives rise to a yellow or brownish incrustation of oxide of lead.

Physiological Effects.—In its metallic state lead seems to be inert. But all the compounds of the metal that are soluble in water or in the animal juices are more or less poisonous. *Acute* poisoning by the preparations of lead has been of rare occurrence, and has chiefly been the result of accident.

Of the salts of lead, the *acetate*, or *sugar of lead*, is one of the most active, and has more frequently been taken as a poison than any of the other compounds. This salt, however, is poisonous only when taken in large quantity. Van Swieten mentions an instance in which it was given to the amount of a drachm daily for ten days before it caused any material symptom. (Christison, *On Poisons*, 430.) Cases are not wanting, however, in which it produced speedy and violent symptoms, and even death.

Acetate of Lead.

Symptoms.—When an overdose of acetate of lead is swallowed, the patient usually experiences at first a nauseous metallic taste in the mouth, with a sense of constriction or burning heat in the fauces and epigastrium. These effects are followed, sooner or later, by severe gastric and abdominal pains, which are generally relieved, but sometimes increased, by pressure; sometimes the pain is constant, at other times intermittent. There is also nausea, and sometimes frequent vomiting of a yellowish or blackish liquid; in some instances the vomiting has been very slight. The thirst is frequently very urgent; the skin cold, but sometimes hot, and generally covered by a clammy perspiration; the countenance anxious; the strength greatly prostrated; the pulse slow and feeble, but often accelerated. In some instances there has been severe and even bloody purging; but generally the bowels are obstinately constipated, there being either no discharge or the matters passed being hard, dry, and black and their discharge attended with pain. Sometimes the limbs become affected with spasms and a sense of constriction. The urine is usually diminished in quantity. The intellect generally remains clear.

Dr. Maschka relates the case of an aged man who had been ill for some days, and when first seen by a physician was suffering from yellowness of the conjunctiva, loss of appetite, eructations, accumulation of phlegm on the chest, and attacks of giddiness. The evacuations were normal, the thirst not increased, pulse 80 to 90, the tongue coated, and the man felt weak. On the following day the weakness and other symptoms had increased; but under the administration of tonics the patient became better. On the evening of the fourth day, however, he became worse; his eyes were fixed, his breathing short and rattling, pulse weak, the extremities cold, and death shortly ensued. Lead in large quantity was found in the contents of the stomach. The quantity of sugar of lead taken just before the increased symptoms preceding death appeared was said to have been 20.12 grammes. (*Med.-Chir. Rev.*, 1872, 265.)

A case is reported in which the death of an infant was caused by the use of a lotion of lead acetate applied for sore nipples. The mother omitted to wash the lotion off before putting the child to the breast. It was seized with violent colic, and died in a few days with the usual symptoms of lead poisoning.

Dr. von Linstow reports (*Viert. f. Gericht. Med.*, Jan. 1874) two cases of fatal poisoning by *lead chromate*, which occurred in children aged respectively one and three-quarters and three and a half years, caused by sucking some pastry colored by chrome yellow. Several hours after the poison had been taken, both children were taken with vomiting, which lasted several hours, the matters vomited having a yellow color. There was great prostration and extreme thirst, but no diarrhœa nor pain. On the second day both had a hot and red countenance, and were stupid. The younger, about twenty-four hours after the commencement of the symptoms, had a slight diarrhœa and convulsions, which continued until death, which took place in forty-eight hours. On the third day an erythematous eruption appeared on the chest and abdomen of the elder, and he was dull and stupid. On the fourth day the pulse and respiration became irregular, the breath extremely fetid, stupor and unconsciousness supervened; and the patient died five days after the ingestion of the poison. The quantity taken in each case was believed to be between the 1–5th and the 1–6th of a grain of the lead compound.

Chronic Poisoning.—It is well known that the frequently re-

peated introduction of even very minute quantities of any of the preparations of lead into the system may after a time induce serious symptoms. Under these circumstances, the patient experiences general depression, loss of appetite, a metallic taste in the mouth, and generally great thirst. The throat becomes dry, the breath fetid, the countenance dull and anxious, the skin dry and of a dull yellow color, the bowels constipated, and the urine generally diminished. At the same time a blue line forms along the margins of the gums; and there is more or less uneasiness or pain in the abdomen. As the case advances, the pain in the abdomen becomes very severe, and more or less constant: the walls of this cavity are generally hard and depressed. These effects are frequently followed by sharp pains in the extremities, muscular emaciation, and paralysis.

A remarkable series of cases of lead poisoning occurred a few years since from the use of flour from a mill in which the millstones had been repaired by filling the defective parts with lead. Of four hundred and twelve persons who suffered from the use of the flour, thirty died. (*Med. Times and Gaz.*, May, 1878.) Other instances similar to this have been reported.

Within recent years a number of cases of lead poisoning have occurred from the use of *canned fruits* preserved in tinned cans alloyed with lead. In a case of this kind reported by Dr. Magruder (*Med. News*, Sept. 1883, 261), there were colic, arthralgia, and paralysis, involving first the extensors of the wrist, and then those of the lower extremities, and extending also to the flexors of both. The lead-cachexia was well marked, and the bluish line on the gums very distinct.

In a case reported by Dr. G. A. Kunkler, the *external* application of white-lead to a scalded surface, as a dressing, produced unmistakable symptoms of lead colic,—acute abdominal pain, retraction of the umbilicus, constipation, and slight discoloration of the gums. (*Med.-Chir. Rev.*, Oct. 1857, 525.) And Dr. G. Johnson, of London, has reported (1875) a very severe case of chronic lead poisoning resulting from the use of *flake-white*, composed chiefly of carbonate of lead, as a cosmetic.

When Fatal.—In a case quoted by Dr. Beck, a soldier who swallowed an unknown quantity of acetate of lead in solution was soon seized with the most violent symptoms, indicative of gastric inflammation, and died in great agony at the end of three days. (*Med.*

Jur., i. 690.) Dr. Taylor refers to two cases in which Goulard's extract—which is a solution of the subacetate of lead—was taken in unknown quantity by two children, aged respectively four and six years, and they both died within thirty-six hours. The symptoms were at first violent vomiting and purging: in one case they resembled those of Asiatic cholera. (*Op. cit.*, 482.) In a case mentioned by Dr. Christison (*On Poisons*, 430) the same preparation of lead was taken in unknown quantity by a soldier. The first symptoms could not be ascertained, but on the second day he was affected with loss of appetite, paleness, costiveness, and excessive debility; on the third day he had severe colic, drawing in of the abdomen, loss of voice, cold sweats, locked jaw, and violent convulsions, and expired before the evening of the same day.

Fatal Quantity.—In the few fatal cases of *acute* poisoning by lead acetate that have occurred, the quantity taken could not be accurately determined. Instances are reported in which doses of about an ounce were taken without producing any very serious results. On the other hand, a case is quoted by Dr. Christison in which two doses of a drachm each taken by a man, with an interval of several hours between the doses, produced acute pain in the abdomen, bilious vomiting, loss of speech, delirium, profuse sweating, and slow pulse: with the aid of treatment the patient recovered. Two cases have already been cited in each of which about the 1–5th of a grain of the chromate of lead proved fatal to two very young children.

Treatment.—In acute poisoning by the acetate of lead, the stomach should be immediately emptied by the administration of an emetic of zinc sulphate, and its action followed by large draughts of milk containing white of egg. Various chemical antidotes have been proposed. Among these the most useful is sulphuric acid in the form of a solution of magnesium or sodium sulphate. Either of these salts would decompose the lead compound, with the formation of insoluble and inert lead sulphate. The alkaline sulphides have also been recommended. They would give rise to the insoluble sulphide of lead. These salts, however, are in themselves poisonous in large doses, and their use as antidotes has not been as successful as upon chemical grounds might have been expected. The hydrated sesquisulphide of iron has been strongly recommended by M. Bouchardat; and its efficacy has been recently confirmed in a case

reported by M. Lepage. As this compound is inert, it may be administered in large quantity. The alkaline carbonates are inadmissible, as they would give rise to lead carbonate, which is equally poisonous with the acetate of the metal. In chronic lead poisoning, M. Rabuteau strongly advises sodium iodide as preferable to the potassium salt.

Post-mortem Appearances.—In the case already cited from Dr. Beck, the mucous membrane of the stomach was found abraded in several places, particularly near the pylorus; and the œsophagus, stomach, duodenum, mesentery, liver, and spleen were in a state of high inflammation. In the two cases mentioned by Dr. Taylor, the mucous membrane of the stomach was found of a gray color, but otherwise perfectly healthy; and the intestines were much contracted. In the fatal case cited by Dr. Christison, the lower end of the œsophagus, the whole stomach and duodenum, part of the jejunum, and the ascending and transverse colon were found much inflamed; and the villous coat of the stomach appeared as if macerated.

It is necessary to bear in mind that acetate of lead has caused death without leaving any well-marked morbid appearance in the body.

In the two cases in which the chromate of lead proved fatal, the mucous membrane of the stomach and duodenum was found swollen and loose, and in some places entirely destroyed, and at one spot perforation had taken place, due to the corrosive action of the poison. There were also found hyperæmia of the brain and its membranes, beginning fatty degeneration of the liver, commencing icterus, hyperæmia of the kidneys, suppurative pyelitis, and a softened condition of the spleen.

Chemical Properties.

General Chemical Nature.—Acetate of lead, as usually found in the shops, is in the form of white crystalline masses, which have a density of about 2.6, a slight vinegar-like odor, and a sweetish, astringent taste. In its crystalline state this salt consists of one atom of lead, two molecules of acetic acid, with three of water, $Pb2C_2H_3O_2$; 3Aq; it crystallizes in four-sided prisms. When the crystals are exposed to dry air they slightly effloresce, and after a time become partially converted into lead carbonate, from the absorption of carbonic acid from the atmosphere. When moderately heated,

they fuse and give off their water of crystallization; at higher temperatures the salt undergoes complete decomposition, leaving a black residue consisting of a mixture of charcoal and metallic lead.

Solubility. 1. *In Water.*—When finely powdered crystallized acetate of lead is agitated for a few minutes with its own weight of water, at a temperature of 15.5° C. (60° F.), and the liquid quickly filtered, crystals of the salt immediately begin to separate from the filtrate; if this mixture be allowed to evaporate spontaneously, it leaves a crystalline residue, indicating that the filtered fluid originally held in solution one part of the salt in 1.62 parts of the liquid.

When the powdered salt is agitated for a few minutes with an equal weight of water at a temperature of 15.5° C. (60° F.), and the mixture allowed to stand at about the same temperature for forty-eight hours, and the liquid then filtered, the filtrate contains only one part of the salt in 2.67 parts of water.

From these experiments it is obvious that the mere act of agitation very much increases the solubility of this salt in water. This circumstance may, in part at least, account for the discrepant statements of observers in regard to the solubility of the salt.

2. *In Alcohol.*—When large excess of the pulverized salt is agitated for a few minutes with pure alcohol of 97 per cent., and the solution quickly filtered, the filtrate contains one part of the salt in twenty parts of the liquid. But if, after agitating the mixture for a few minutes, it be allowed to stand quietly for twenty-four hours and the liquid then filtered, the filtrate contains only one part of the salt in about sixty-five parts of the menstruum.

The more dilute the alcohol, other conditions being equal, the greater will be the quantity of the salt that it will dissolve.

3. *In Ether.*—Absolute ether, under any circumstance, fails to dissolve an appreciable trace of the salt.

Special Chemical Properties.—When acetate of lead, in its solid state, is moistened with a solution of potassium iodide, it assumes a bright yellow color, due to the formation of iodide of lead. The least visible quantity of the salt will exhibit this reaction. Thus, a residue representing only 1–1000th of a grain of lead oxide will yield a very satisfactory bright yellow coloration; and even the 1–10,000th of a grain, when deposited at one point, will assume a distinct yellow hue. The lead iodide thus produced is slowly soluble in large excess of the reagent.

If a small portion of the salt be introduced into a drop of potassium chromate solution, it also assumes a bright yellow color, lead chromate being formed. Crushing the crystal facilitates the formation of the yellow compound.

When gradually heated on a piece of porcelain, acetate of lead fuses to a clear liquid, boils, and then becomes reduced to a white, anhydrous mass; if the heat be continued, the mass again fuses, then becomes dry and charred, and slowly assumes a yellowish or reddish-brown color. This residue consists of a mixture, in variable proportions, of different oxides of lead. Almost the least visible crystal of the salt, when thus treated, leaves a brownish residue, apparently several times greater than the crystal employed. The carbonate of lead, when treated in this manner, does not fuse; but it is slowly decomposed, with the production of a similar reddish-brown residue.

Heated upon a piece of charcoal in the inner blow-pipe flame, acetate of lead fuses, then undergoes decomposition, with the production of bright, malleable globules of metallic lead, and the formation of a yellow incrustation of oxide of lead. The carbonate of lead, under these circumstances, yields at first a brownish mass, which soon furnishes bright, metallic globules.

When acetate of lead is placed in a small quantity of ferric chloride solution, it slowly dissolves to a fine red solution of ferric acetate, $Fe_26C_2H_3O_2$. If the salt be heated in a test-tube with concentrated sulphuric acid, it undergoes decomposition, with the evolution of pungent vapors of acetic acid. When heated with a mixture of equal volumes of alcohol and sulphuric acid, it evolves acetic ether, readily recognized by its peculiar aromatic odor. These reactions are simply due to the acetic acid of the lead salt, and are common to all acetates.

Pure aqueous solutions of lead acetate are colorless, odorless, and have a sweetish, styptic taste, and, if not too dilute, a feebly acid reaction. When a solution of this kind is allowed to evaporate spontaneously, the salt is left in the form of white, crystalline needles.

In the following examinations in regard to the behavior of reagents with solutions of lead, the pure crystallized acetate was dissolved in water very slightly acidulated with acetic acid. The fractions employed indicate the fractional part of a grain of lead oxide, PbO, or its equivalent, in solution in one grain of the liquid.

Except when otherwise indicated, the results refer to the behavior of one grain of the solution. One part of lead oxide represents 1.696 parts of crystallized acetate of lead.

1. *Sulphuretted Hydrogen.*

This reagent, either in its gaseous state or in the form of an alkaline sulphide, throws down from *neutral*, *acidulated*, and *alkaline* solutions containing lead a black, amorphous precipitate of lead sulphide, PbS, which is insoluble in the caustic alkalies and in the diluted mineral acids. Hot concentrated hydrochloric acid dissolves the precipitate, with the evolution of sulphuretted hydrogen and the formation of lead chloride, which, unless the quantity be very minute, separates, as the liquid cools, in the form of beautiful crystalline plates.

The precipitate is readily decomposed by hot nitric acid, with the formation of lead nitrate and the separation of free sulphur; if the acid be concentrated and the heat continued, the separated sulphur becomes oxidized into sulphuric acid, which, displacing the nitric acid, unites with the lead, forming lead sulphate. The sulphate of lead thus formed generally separates in the form of a white, granular powder, but sometimes in the form of small, brilliant crystalline plates; if, however, the quantity of the lead salt produced be only small, it may remain in solution in any excess of nitric acid present.

In examining the limit of the reaction of this reagent, a slow stream of the washed sulphuretted gas was passed into *ten grains* of the lead solution, contained in a small test-tube.

1. 1–100th solution ($= \frac{1}{100}$th grain PbO) yields an immediate, copious, black deposit. When the precipitate is dissolved in the mixture, by excess of hydrochloric acid, it yields a white precipitate of crystalline needles of lead chloride.
2. 1–1000th solution yields an immediate precipitate. When a solution of this strength is exposed to the vapor of sulphuretted hydrogen, its surface becomes covered with a black pellicle of lead sulphide.
3. 1–10,000th solution: the first bubble of the reagent produces a deep brown coloration; and a few bubbles produce a deep brown turbidity. After saturating the solution with the reagent, and

allowing it to stand an hour, a very satisfactory black deposit separates.

4. 1–50,000th solution: after a few moments the liquid assumes a distinct brown color, and very soon presents a brown turbidity; after a few hours distinct brownish flakes separate.
5. 1–100,000th solution: after some minutes the liquid assumes a distinct brownish tint, and soon afterward becomes turbid: after some few hours the brownish color deepens, but no deposit separates.
6. 1–250,000th solution: after several minutes the liquid assumes a just perceptible cloudiness, with a faint brownish tint, which is only distinctly observed when compared with a clear solution, and best seen by looking through the liquid from the top.

The formation of the precipitate from very dilute solutions is much facilitated by heating the mixture. The delicacy of the reaction of this test has been variously stated. Thus, Pfaff placed the limit of the brown coloration at one part of lead oxide, in the form of nitrate, in 100,000 parts of liquid; Lassaigne, at 200,000 parts; and Harting, at 350,000 parts. As, however, neither of these observers states the amount of the solution operated upon, these discrepancies are readily explained.

Fallacies.—The production of a black precipitate by this reagent is common to solutions of several other metals besides lead. The true nature of the lead precipitate may be established by dissolving it, by the aid of heat, in diluted nitric acid containing just sufficient of the acid to effect decomposition, and then testing the solution with either potassium iodide or potassium chromate, or with diluted sulphuric acid; or, after filtration, the nitric acid solution may be evaporated to dryness, and the residue examined by any of the tests already mentioned for salts of the metal when in the solid state.

When strongly heated in a reduction-tube, lead sulphide is converted into a hard, brittle mass, but fails to yield a sublimate.

2. *Sulphuric Acid.*

This acid and its soluble salts throw down from solutions of salts of lead a heavy, white precipitate of lead sulphate, $PbSO_4$, which is soluble in large excess of the fixed alkalies, and in some of the salts of ammonium, but very sparingly soluble in diluted nitric and hydrochloric acids. Strong nitric acid dissolves it in limited quantity

to a clear solution. Concentrated hydrochloric acid dissolves it rather readily, especially upon the application of heat, yielding crystals of lead chloride as the mixture cools.

From very dilute solutions of salts of lead the precipitated sulphate does not separate until after some time: it then deposits in the form of small granules. Solutions of the alkaline carbonates, normal and acid, convert lead sulphate, even at ordinary temperatures, into lead carbonate; solutions of normal alkaline carbonates, but not those of the acid carbonates, dissolve some of the lead compound in this process (H. Rose). From an alkaline solution of lead sulphate the metal is precipitated by sulphuretted hydrogen as lead sulphide.

1. $\frac{1}{100}$ grain of lead oxide, or its equivalent, in one grain of liquid, yields with a drop of dilute sulphuric acid a copious precipitate, which partly consists of crystalline needles. If the drop of reagent be allowed to flow slowly into the lead solution, the precipitate generally consists of a mass of crystalline needles, Plate V., fig. 3.
2. $\frac{1}{1000}$ grain yields a good precipitate, consisting principally of needles and granules.
3. $\frac{1}{5000}$ grain: an immediate granular precipitate, and in a little time a quite fair deposit.
4. $\frac{1}{10,000}$ grain: after a few moments a cloudiness appears, and in a little time there is a very satisfactory granular deposit.
5. $\frac{1}{20,000}$ grain yields after a few moments a slight cloudiness, and after a little time a satisfactory granular precipitate.

If potassium sulphate be employed as the reagent, it produces the same results as the above.

Free sulphuric acid, as well as soluble sulphates, also produces white precipitates in solutions of barium and strontium salts. The lead sulphate, however, is distinguished from that of either of these metals, in that when moistened with ammonium sulphide it is turned black, due to the formation of lead sulphide. When lead sulphate is intimately mixed with sodium carbonate and heated before the blow-pipe flame, on a charcoal support, it yields globules of metallic lead.

3. *Hydrochloric Acid.*

Hydrochloric acid and its soluble salts occasion in somewhat strong solutions of lead salts a white precipitate of lead chloride,

$PbCl_2$, which is less soluble in diluted hydrochloric and nitric acids than in pure water. When excess of lead chloride is digested, at the ordinary temperature, with *pure* water for forty-eight hours, one part of the salt dissolves in 110 parts of the liquid: it is much more soluble in hot water. It is readily soluble in concentrated hydrochloric acid. Chloride of lead bears a strong heat without decomposition; but at higher temperatures, with a free supply of air, it is partially decomposed, with the evolution of chlorine, and leaves a residue consisting of a mixture of oxide and chloride of lead.

1. $\frac{1}{100}$ grain of lead oxide, in one grain of water, yields, with free hydrochloric acid, a copious, white crystalline precipitate, Plate V., fig. 4.
2. $\frac{1}{500}$ grain: in a very little time a very fair deposit of granules and crystalline needles.
3. $\frac{1}{1000}$ grain yields after some minutes a quite satisfactory deposit of granules, needles, and prisms.

The results under 2 and 3 are obtained only when excess of hydrochloric acid is employed.

This reagent, as well as soluble chlorides, also produces white precipitates in solutions of silver and of mercurous salts. The chlorides of silver and mercury, however, are always thrown down in the amorphous form. The precipitated lead chloride is insoluble, and unchanged in color, by caustic ammonia; whereas the silver precipitate is readily soluble in that alkali, whilst the mercury compound is turned black. The action of ammonia, therefore, readily serves to distinguish between the chlorides of these three metals. Moreover, the lead chloride is readily soluble, especially by the aid of heat, in large excess of water, whereas, on the other hand, the silver chloride and mercurous chloride are wholly insoluble in this liquid.

4. *Potassium Iodide.*

This reagent produces in solutions of salts of lead a bright yellow precipitate of lead iodide, PbI_2, which is readily soluble to a clear solution in potassium hydrate, but almost wholly insoluble even in very large excess of the precipitant; under the action of ammonia it slowly assumes a white color. It dissolves to a clear solution in strong hydrochloric acid; nitric acid dissolves it to lead nitrate. Heated before the blow-pipe, on charcoal, it turns reddish-yellow, then becomes brownish, and finally volatilizes.

Iodide of lead is but sparingly soluble in cold water, but at the boiling temperature it dissolves more freely, and separates, as the liquid cools, in beautiful, six-sided laminæ. We have found that when excess of the well-washed salt is digested in pure water, with frequent agitation for twenty-four hours, at a temperature ranging from 15° to 21° C. (60° to 70° F.), one part dissolves in 1528 parts of the fluid. It is, however, much less soluble in a dilute solution of potassium iodide. This reagent, therefore, produces a copious precipitate from a pure saturated aqueous solution of lead iodide; even in the presence of slight excess of the reagent a precipitate will form when the lead iodide does not form more than the 1–10,000th part by weight of the solution. The precipitate from a 1–1000th solution of lead oxide does not usually entirely dissolve by heating the mixture to the boiling temperature.

1. $\frac{1}{100}$ grain of lead oxide yields a copious, bright yellow precipitate, which is usually partly granular and crystalline.
2. $\frac{1}{1000}$ grain yields a very good deposit.
3. $\frac{1}{2500}$ grain yields a quite good precipitate, which readily dissolves by heating the mixture to the boiling temperature, and again separates, as the liquid cools, in brilliant, golden-yellow, six-sided plates, Plate V., fig. 5.
4. $\frac{1}{5000}$ grain: a very fair deposit.
5. $\frac{1}{10,000}$ grain yields an immediate yellow precipitate, which soon becomes a fair deposit.
6. $\frac{1}{20,000}$ grain yields, with a very small quantity of the reagent, after a little time, a quite satisfactory deposit of granules and small plates.

The production, by this reagent, of a yellow precipitate, which is soluble in boiling water, and separates as the mixture cools, in the form of six-sided plates, is characteristic of lead.

5. *Potassium Chromate.*

Potassium chromate and the dichromate throw down from solutions of salts of lead a bright yellow, amorphous precipitate of lead chromate, $PbCrO_4$, which is insoluble in acetic acid, and only sparingly soluble in diluted nitric acid, but readily soluble in potassium hydrate. Hydrochloric acid slowly changes it to white lead chloride; it is blackened by ammonium sulphide.

1. $\frac{1}{100}$ grain of lead oxide yields a copious precipitate.

2. $\frac{1}{1000}$ grain: a very good deposit.
3. $\frac{1}{10,000}$ grain yields a quite good, greenish-yellow precipitate.
4. $\frac{1}{50,000}$ grain yields an immediate cloudiness, and in a few minutes a very satisfactory greenish deposit.
5. $\frac{1}{100,000}$ grain yields after a little time a greenish turbidity.

The formation of the deposit from dilute solutions is facilitated by heating the mixture.

Potassium chromate produces in dilute neutral solutions of salts of copper a yellowish precipitate, which after a time assumes a reddish-brown color, and which, unlike the lead chromate, is readily soluble in acetic acid. The precipitate from somewhat strong solutions of copper has at once a reddish-brown color. Potassium dichromate produces no precipitate from even concentrated solutions of salts of copper.

6. *Potassium Hydrate and Ammonia.*

The caustic alkalies produce in solutions of salts of lead a white precipitate, consisting chiefly of the hydrated oxide of lead, which is readily soluble in large excess of the fixed alkalies, insoluble in ammonia, and but sparingly soluble in ammonium nitrate. The precipitate is readily soluble in nitric acid, and is changed to lead chloride by hydrochloric acid. Upon the addition of sulphuretted hydrogen or ammonium sulphide, the precipitate is changed to black sulphide of lead.

From solutions of acetate of lead ammonia causes only a partial precipitate, due to the formation of triplumbic acetate (tribasic acetate of lead), $2PbO$; $Pb_2C_2H_3O_2$, which remains in solution.

1. $\frac{1}{100}$ grain of lead oxide yields with either of the fixed alkalies a copious, white, amorphous deposit.
2. $\frac{1}{1000}$ grain: a very good precipitate, which is readily soluble in excess of the precipitant.
3. $\frac{1}{10,000}$ grain yields with a very small quantity of the reagent a very satisfactory deposit.

These reagents also produce white precipitates with solutions of several other metals, which in some instances, as with bismuth and tin, are, like the lead deposit, blackened by ammonium sulphide. When, however, the dried lead precipitate is heated on charcoal before the reducing flame of the blow-pipe, it leaves malleable metallic globules, which are characteristic of this metal.

7. *Alkaline Carbonates.*

The alkaline carbonates occasion in solutions of salts of lead a white amorphous precipitate of lead carbonate, together with more or less hydrated oxide of the metal. The precipitate is almost wholly insoluble in excess of the precipitant, but readily soluble in nitric and acetic acids, and is changed to lead chloride by hydrochloric acid; it is also readily soluble in large excess of the fixed caustic alkalies.

1. $\frac{1}{100}$ grain of lead oxide, in one grain of water, yields a copious precipitate.
2. $\frac{1}{1000}$ grain: a very good deposit.
3. $\frac{1}{10,000}$ grain: a very satisfactory precipitate.
4. $\frac{1}{50,000}$ grain yields within a few minutes a quite distinct cloudiness.

These reagents also produce white precipitates in solutions of many other metals. But from all these precipitates the lead compound is readily distinguished by its behavior before the blow-pipe flame.

8. *Ammonium Oxalate.*

This reagent produces in neutral solutions of salts of lead a white precipitate of lead oxalate, which soon becomes crystalline. The precipitate is readily soluble in nitric acid, but insoluble in acetic acid, and blackened by ammonium sulphide.

1. $\frac{1}{100}$ grain of lead oxide yields a copious precipitate, which soon changes to a mass of long crystalline needles.
2. $\frac{1}{1000}$ grain yields a very good deposit, which soon changes to granules and groups of needles.
3. $\frac{1}{10,000}$ grain yields an immediate cloudiness, and after a little time a quite distinct deposit.
4. $\frac{1}{50,000}$ grain yields after some minutes a quite satisfactory turbidity.

When lead oxalate is heated before the blow-pipe on a charcoal support, it yields globules of metallic lead.

9. *Zinc Test.*

When a drop of a solution of acetate of lead is placed in a watch-glass, and a fragment of bright zinc added, the lead com-

pound is slowly decomposed, with the deposition of metallic lead upon the zinc, in the form of a brush-like, crystalline deposit. If the lead solution be placed upon a piece of bright copper and the metal touched through the drop with a needle of zinc, the lead deposits partly on the zinc and partly on the copper, as a strongly adhering, gray deposit, over the space occupied by the drop.

1. $\frac{1}{100}$ grain of lead oxide, when placed in a watch-glass and treated as just stated, yields a quite large, brush-like deposit.
2. $\frac{1}{1000}$ grain: the zinc immediately darkens, and in a little time receives a quite satisfactory deposit.

A solution of *tin* yields with a fragment of zinc a brush-like deposit of metallic tin, which sometimes very closely resembles that produced under similar conditions by lead.

Potassium ferrocyanide produces in solutions of salts of lead a white amorphous precipitate of ferrocyanide of lead, Pb_2FeCy_6, which is slowly soluble in large excess of nitric acid, and changed to lead chloride by hydrochloric acid. One grain of a 1–1000th solution of lead oxide yields with this reagent a quite good precipitate; and the same quantity of a 1–10,000th solution gives after a little time a quite satisfactory deposit.

Potassium ferricyanide throws down from solutions of acetate of lead a dirty-yellow precipitate, which is soluble in nitric acid, decomposed by hydrochloric acid, and blackened by ammonium sulphide. With one grain of a 1–1000th solution of lead oxide the reagent produces a quite good amorphous deposit; one grain of a 1–10,000th solution yields after a few minutes a quite satisfactory granular precipitate.

Both these reagents produce somewhat similar precipitates in solutions of several other metals.

Separation from Organic Mixtures.

Suspected Solutions.—Various kinds of animal and vegetable substances more or less decompose and precipitate acetate of lead when in solution; but most of these precipitates are readily soluble in diluted nitric acid. When a mixture of this kind is presented for examination, it should be acidulated with nitric acid and heated for some time, then allowed to cool, the liquid filtered, and the solids upon the filter washed, the washings being collected with the

original filtrate, and the solids reserved. The filtrate, after concentration if necessary, is then saturated with sulphuretted hydrogen gas, and the mixture allowed to stand in a moderately warm place for some time; any precipitate thus produced is collected on a small filter, washed, and, while still moist, washed from the filter into a test-tube or any convenient vessel, by means of a jet of water from a wash-bottle.

When the precipitate has completely subsided, most of the supernatant fluid is decanted, and the solid residue dissolved, by the aid of a gentle heat, in the least possible quantity of nitric acid, added drop by drop. By this means any lead sulphide present will be converted into lead nitrate, while the sulphur set free will remain unoxidized. The mixture is now diluted somewhat with pure water, the liquid filtered, and a portion of the filtrate tested with a solution of potassium chromate. Other portions of the filtrate may be examined by any of the other tests already pointed out.

The sulphide of lead precipitated from the 1–1000th of a grain of lead oxide, when diffused in ten grains of water and heated with one drop of nitric acid, yields a clear solution, which gives with reagents about the same reactions as a 1–10,000th solution of lead oxide. If large excess of nitric acid has been used for dissolving the lead sulphide, the filtered liquid should be carefully neutralized by pure potassium hydrate before the application of any of the tests.

It would rarely, if ever, happen with organic mixtures of this kind containing lead that the metal would entirely escape solution in diluted nitric acid. If, however, there has been a failure to detect the metal by the above method, the solids obtained by filtration from the original mixture may be boiled for some time with water containing about one-sixth of its volume of nitric acid, the solution filtered, the filtrate evaporated to dryness, and the residue incinerated. This residue is treated with a little nitric acid, the solution diluted with a small quantity of water, then filtered, and the filtrate neutralized and tested in the ordinary manner.

Contents of the Stomach.—These, after the addition of water if necessary, may be acidulated with nitric acid, and examined in the manner just described for suspected solutions.

If an alkali sulphate had been administered as an antidote, the poison may be in the form of insoluble lead sulphate. Under these circumstances, the contents of the stomach should be carefully exam-

ined, and any white powder found collected and washed, then boiled with a strong solution of pure caustic potash, and the lead precipitated by sulphuretted hydrogen. Or, any lead sulphate obtained may be placed in a wide test-tube and agitated occasionally for several hours with a strong solution of acid sodium carbonate, the clear liquid decanted, and the operation repeated with a fresh portion of the sodium solution. By this means the lead sulphate will be converted into insoluble lead carbonate. This is washed, then dissolved in a little acetic acid or in very dilute nitric acid, and the solution tested.

According to the observations of Orfila, in acute poisoning by the salts of lead, the villous coat of the stomach frequently presents numerous white points which contain lead, and which are blackened by sulphuretted hydrogen.

From the Tissues.—The solid organ, such as a portion of the liver, is cut into small pieces and boiled in a porcelain dish with nitric acid, diluted with about four parts of water, until the mixture becomes homogeneous. When the mixture has cooled, the liquid is filtered, the filtrate evaporated to dryness, the residue moistened with nitric acid, again evaporated to dryness, and the heat continued until all vapors cease to be evolved and the residue becomes a carbonaceous mass. The mass thus obtained is pulverized and boiled with a small quantity of strong nitric acid, the mixture diluted with water, the solution filtered, the filtrate evaporated to dryness, and the residue dissolved in a small quantity of water slightly acidulated with nitric acid. This solution, after filtration if necessary, is saturated with sulphuretted hydrogen gas, and allowed to stand until the precipitate has completely subsided. Any lead sulphide thus deposited is collected on a small filter, washed, then suspended in a small quantity of water and dissolved, by the aid of heat, in the least possible quantity of nitric acid, and the solution tested in the usual manner.

If the quantity of lead sulphide precipitated by the sulphuretted gas is too minute to be separated from the filter, the filter, or that portion of it containing the deposit, may be heated with sufficient dilute nitric acid to dissolve the precipitate; the solution is then filtered, neutralized, and tested.

From the observations of several experimentalists, it appears that absorbed lead is very slowly eliminated from the system. Orfila

states (*Toxicologie*, i. 858) that when dogs were given about eight grains of acetate of lead daily for one month, the metal was found in the liver and brain of the animals when killed one hundred and four days after they had ceased to take the poison. According to this observer, the metal is eliminated from the body principally with the urine.

From the Urine.—Fifteen or twenty ounces of the urine, acidulated with nitric acid, may be evaporated to dryness, the residue carbonized by nitric acid, and the carbonaceous mass treated in the manner just described for the separation of the metal from the tissues. By following this method we detected the metal in notable quantity in the urine almost daily for about two weeks, in two instances of severe chronic lead poisoning resulting from the use of water collected in a leaden cistern. Of eight persons who used this water, only two were affected by it, and these the elder members of the family.

Kletzinsky proposes, after rendering the urine alkaline by potassium hydrate, to add about two per cent. of its weight of potassium nitrate and evaporate to dryness. The residue is then exposed to a dull red heat, whereby the whole of the organic matter is destroyed. The cooled mass is powdered and boiled for some time with a half-saturated solution of neutral ammonium tartrate, to which some caustic ammonia has been added, the solution filtered, the filtrate acidulated with hydrochloric acid, and then precipitated by sulphuretted hydrogen. The precipitate is allowed twenty-four hours to subside, then washed, redissolved in warm *dilute* nitric acid, and the solution filtered, neutralized, and tested in the usual manner. (Thudichum, *On the Urine*, 406.)

Quantitative Analysis.—Lead may be very accurately estimated in the form of sulphide of the metal. The solution, very slightly acidulated with nitric acid, is treated with a slow stream of washed sulphuretted hydrogen gas as long as a precipitate is produced, and the mixture then allowed to stand in a moderately warm place until the precipitate has completely deposited. The precipitate is collected on a filter of known weight, washed, thoroughly dried on a water-bath, and weighed. One hundred parts by weight of the dried sulphide correspond to 86.19 parts of metallic lead, or 93.33 of lead oxide, or 158.37 of pure crystallized acetate of lead.

When the lead exists in the form of sulphate, this may be washed with water containing a little alcohol, dried at 100° C. (212° F.), and weighed. One hundred parts by weight of the dried sulphate correspond to one hundred and twenty-five parts of crystallized acetate of lead.

Section II.—Copper.

History and Chemical Nature.—Copper is represented by the symbol Cu; its atomic weight is 63.4, and its specific gravity 8.95. This metal is frequently found in its uncombined state in nature; its most common ore is copper pyrites, which consists of a mixture of the sulphides of copper and iron. According to Walchner, copper is as widely distributed in nature as iron. In some mineral waters it is said to exist to the extent of half a grain to the gallon of water. It is also found in sea-water and in sea-weeds. Sarzeau states that he found it in minute quantity in various vegetable substances, such as coffee, sugar, wheat, and flour; and minute traces of it have been found in the blood and various organs of the healthy human body. In fourteen human bodies examined by Dr. G. Bergeron, the metal was found in the liver in each case, but in no instance did the amount exceed about one milligramme (1–65th grain) in the entire liver. (*Jour. de Chim. Méd.*, Nov. 1874, 503.) In the ash obtained from a million parts of grain and of flour, Dr. Van den Berghe found from eight to eleven parts of copper. (*Chem. Zeit.*, March, 1882, 223.)

Copper, in its uncombined state, is a rather hard, quite tough, ductile metal, of a peculiar red color, and a somewhat granular fracture; its fusing point, according to Daniell, is about 1091° C. (2000° F.). When exposed to moist air, it slowly absorbs oxygen and carbonic acid, with the formation of a green coating of hydrated oxycarbonate of copper, $CuO,CuCO_3,H_2O$, known also as *natural verdigris*. Immersed in pure water, copper undergoes little or no change; but in water containing common salt it slowly becomes covered with a layer of oxychloride of the metal. In water containing an organic acid, as vinegar, or when certain kinds of fatty matters are present, the metal is more readily acted upon. Nitric acid rapidly dissolves it, with the evolution of nitrogen dioxide and the formation of copper nitrate. Cold sulphuric acid has no direct action upon the metal; but the hot acid readily dissolves it, with the evolution of sulphu-

rous oxide gas (SO_2), to copper sulphate. Hydrochloric acid, even at the boiling temperature, fails to act upon the metal.

Combinations.—Copper readily unites with most of the non-metallic elements. With oxygen it unites in two proportions, forming the monoxide (CuO) and the suboxide (Cu_2O), the former of which has a black, and the latter a red, color. In its hydrated state the monoxide has a blue color; the color of the hydrated suboxide is yellow. The monoxide of copper readily unites with acids, forming salts known as the cupric salts, which in their hydrated state have either a blue or a green color, and several of which are freely soluble in water. The suboxide forms but few salts, and these are quite unstable. The most important compounds of copper, in regard to their medico-legal relations, are the sulphate and the subacetate, or verdigris.

Sulphate of copper, or *blue vitriol*, in its crystallized state, has the composition $CuSO_4,5Aq$, its molecular weight being 249.4. In this state it forms large blue crystals, which have a nauseous metallic taste, and a density of 2.27. It is soluble in between two and three times its weight of water at the ordinary temperature, and in less than its own weight of boiling water: the solution has a blue color, and a distinctly acid reaction. At a temperature of about 204° C. (400° F.) the salt becomes anhydrous and crumbles to a nearly white powder; at a strong red heat it undergoes decomposition, evolving free oxygen and sulphurous oxide, and leaving a residue of copper monoxide.

Verdigris, as found in the shops, is a mixture in variable proportions of the lower acetates of copper, having either a blue or a green color, and a disagreeable acetous odor. It is usually met with in the form of hard, irregular masses, but sometimes as a fine powder. Under the action of water verdigris is only partly dissolved, a greenish residue of tribasic oxyacetate of copper ($2CuO$; $Cu2C_2H_3O_2$) being left. It is completely soluble in water containing a little free hydrochloric or nitric acid. Sulphuric acid readily decomposes it, with the formation of copper sulphate and the elimination of acetic acid.

Physiological Effects.—When swallowed in its metallic state, copper seems to be entirely inert, at least so long as it retains its metallic form; should, however, the metal become oxidized within the alimentary canal, it may give rise to severe symptoms. In a case quoted by Dr. Beck, in which six copper penny-pieces were swallowed

and retained in the body for five years, no inconvenience was experienced except the effects of mechanical obstruction. On the other hand, a case is related by Dr. Jackson, of Boston, in which a copper half-cent swallowed by a child produced nausea and vomiting, with other symptoms of copper poisoning.

The compounds of copper, when taken in large doses or in frequently repeated small doses, are all more or less poisonous. Even some of the compounds that are insoluble in water are capable of producing very active effects. The preparations of this metal have been rarely administered for criminal purposes; but numerous instances are recorded of accidental poisoning by some of them, resulting from the use of food prepared in copper vessels.

Symptoms.—The usual effects produced by the preparations of copper when swallowed in poisonous quantity are a coppery taste in the mouth, nausea, a sense of burning heat in the mouth and throat, eructations, severe headache, violent vomiting, with more or less purging, and acute pain throughout the stomach and bowels. The pulse becomes small, frequent, and irregular; and there may be great dizziness, difficulty of breathing, great anxiety, cold sweats, extreme thirst, cramps in the extremities, scantiness or entire suppression of urine, and death is sometimes preceded by convulsions and insensibility. Among the symptoms occasionally present is jaundice. Dr. Maschka observed this symptom in a case in which death ensued on the third day, and he attributes it to fatty degeneration of the liver, as in arsenic and phosphorus poisoning.

When taken in frequently repeated small doses, the preparations of copper produce much the same symptoms as those just described. There is loss of appetite; a coppery taste in the mouth; nausea, with frequent efforts to vomit; violent headache; irregular and frequent pulse; hot skin; impaired respiration; great thirst; extreme debility; sharp, shooting pains in the stomach, with tension and tenderness of the abdomen; frequent purging, the discharges being usually dark-colored and their passage attended with pain; and there is more or less alteration of the color of the skin.

A not unfrequent cause of slow poisoning by copper, as already intimated, is the use of utensils of the metal for the preparation of food. The risk of contamination in these cases is always much increased by the free action of the atmosphere, and by allowing the food to cool and remain in contact with the vessel. By employing bright

vessels, and removing the food as soon as prepared, there is little danger in the use of the metal for such purposes.

An instance is related in which ten persons partook of soup prepared in a copper vessel that had not been properly cleaned. They all speedily suffered most violent symptoms, and five of the persons died from its effects within several hours after the soup had been taken. (*Jour. de Chim. Méd.*, July, 1870, 334.)

Period when Fatal.—The time at which death has taken place, in acute poisoning by copper, has been subject to considerable variation. In the case of a young lady, mentioned by Dr. Percival, death occurred on the ninth day. In this case the poisoning resulted from the eating of pickles contaminated with copper. The symptoms were sharp pains in the stomach, an eruption over the breast, general shooting pains, thirst, a small, frequent pulse, vomiting, hiccough, and purging: there were neither convulsions nor stupor. In a case related by Pyl, two ounces of verdigris proved fatal in three days to a woman. In another instance, quoted by Dr. Christison, a lady and her daughter were poisoned by sour-krout which had been kept in a copper vessel. They were soon seized with pain in the stomach, then nausea and vomiting, followed by purging, convulsions, and insensibility. The daughter died in twelve hours, and the mother an hour later. (*On Poisons*, 362.) A child, aged sixteen months, swallowed an unknown quantity of solid sulphate of copper, and died from its effects *four hours* afterward. This is perhaps the most rapidly fatal case yet recorded.

Fatal Quantity.—In a case quoted by Dr. Beck, one ounce of sulphate of copper, taken with suicidal intent by a man aged forty years, proved fatal within twelve hours. (*Med. Jur.*, ii. 667.) In another instance, seven drachms of the same salt, with three drachms of sulphate of iron, caused the death of an adult in three days. Dr. Percival states that the most violent convulsions he ever witnessed were produced in a young woman by two drachms of blue vitriol: under appropriate treatment she recovered. In a case cited by Dr. Taylor, half an ounce of verdigris destroyed the life of a woman in sixty hours; and in another, about twenty grains of the subchloride of copper caused the death of a child. (*On Poisons*, 524.)

On the other hand, Dr. Vergely reports a case (*Jour. de Chim. Méd.*, April, 1873, 152) in which a woman, aged thirty-two years,

drank a solution of fifteen grammes (about two hundred and thirty-two grains) of copper sulphate, and speedily experienced violent symptoms of copper poisoning; but under active treatment she entirely recovered within a few days. And in a case quoted by Dr. A. Stillé (*Mat. Med.*, i. 325), in which an ounce of blue vitriol had been swallowed with suicidal intent, complete recovery took place, although the patient refused to take an emetic.

Treatment.—In acute poisoning by any of the preparations of copper, the vomiting should be encouraged by the free administration of demulcent liquids; or the stomach may be emptied by means of the stomach-pump. As a chemical antidote, albumen in large excess was strongly advised by Orfila. The white of egg should be freely given, and its exhibition followed by large draughts of tepid water. An excess of albumen readily decomposes the soluble salts of copper, with the formation of albuminate of copper, which is said to be but sparingly soluble in the juices of the stomach.

According to the experiments of Dr. Schrader, of Göttingen, milk is equally efficient with albumen as an antidote. The caseate of copper thus produced should be speedily removed from the stomach by vomiting. (*Amer. Jour. Med. Sci.*, Oct. 1855, 540.) M. Duval strongly advised the use of sugar; but it is very questionable whether this substance can be regarded as an antidote: it might, however, be administered in connection with albumen or milk.

Among the other substances that have been proposed as antidotes may be mentioned potassium ferrocyanide, iron filings, calcined magnesia, and hydrated sulphide of iron. The employment of the alkaline sulphides, and also of vinegar, would be inadmissible.

Post-mortem Appearances.—The morbid appearances in poisoning by the preparations of copper are usually confined to the alimentary canal. In acute cases, the inside of the stomach and of the intestines not unfrequently presents a bluish or greenish appearance, due to the presence of the poisonous compound. It should be remembered, however, as first pointed out by Orfila, that a somewhat similar appearance may result from the presence of altered bile. The lining membrane of the stomach is usually inflamed and softened; and in some few instances it presented an ulcerated, and even gangrenous, appearance. Similar appearances have been found in the intestines; in some few cases the intestines were found per-

forated, and their contents had partially escaped into the cavity of the abdomen.

In the fatal case cited by Dr. Beck, the œsophagus was found of a livid-red color, and the stomach of a bluish hue, which could be removed by washing; under this, the mucous membrane was of a deep red color. The intestinal tube, throughout its whole extent, was highly inflamed. In the case before referred to, in which seven drachms of sulphate of copper, together with three drachms of green vitriol, had been taken, the mucous membrane throughout the stomach and intestines was found in a perfectly healthy condition.

Chemical Properties.

In the Solid State.—The general chemical nature and properties of the sulphate and subacetates of copper, or verdigris, have already been pointed out. The nitrate of copper has a beautiful blue color, and is freely soluble in water. The carbonates of the metal have either a blue or a green color; these salts are insoluble in water, but readily soluble in diluted acids, with effervescence. With chlorine the metal unites in two proportions, forming cuprous chloride (Cu_2Cl_2) and the dichloride, or cupric chloride ($CuCl_2$); the former of which is white and insoluble, while the latter has a green color and is readily soluble.

The property of forming blue and green compounds is somewhat peculiar to copper; yet some of the preparations of a few other metals have one or the other of these colors. Thus, some of the compounds of nickel, sesquioxide of chromium, and uranium oxide are green, while some of the salts of cobalt are blue. Copper, however, is the only one of these metals likely to be met with in medico-legal investigations, and is readily distinguished from the others in that when its salts are moistened with a diluted acid and placed in contact with a piece of bright iron or steel, they impart to the iron a coating of metallic copper, readily recognized by its peculiar red color.

Salts of copper, when heated in the inner blow-pipe flame, impart a beautiful green coloration to the outer flame. When mixed with dry sodium carbonate or potassium cyanide and heated on a charcoal support, in the reducing blow-pipe flame, they yield red particles of metallic copper.

Of Solutions of Copper.—The soluble salts of copper com-

municate their color to solutions, even when highly diluted. In the case of the sulphate, the blue color is quite perceptible in fifty grains of a solution containing only 1–1000th of its weight of oxide of copper; the same quantity of a 1–5000th solution exhibits a slight bluish tint. In larger quantities of the liquid, the color of this salt is quite perceptible in solutions much more dilute than those just mentioned. Solutions of salts of copper, when not too dilute, slightly redden blue litmus-paper; they have an astringent, metallic taste, and, when evaporated spontaneously, leave the salt in its crystalline state.

In the following investigations of the different tests for copper when in solution, pure aqueous solutions of the sulphate were employed. The fractions indicate the quantity of *monoxide of copper*, CuO, or its equivalent, present in *one grain* of the solution. One part of the oxide corresponds to 3.141 parts of pure crystallized sulphate of copper.

1. *Sulphuretted Hydrogen.*

Sulphuretted hydrogen gas and the alkaline sulphides throw down from solutions of salts of copper, even in the presence of a free acid, a precipitate of copper sulphide, CuS, which as first produced has a brown color, but sooner or later becomes brownish or greenish-black. The precipitate is slightly soluble in large excess of ammonium sulphide, but insoluble in the fixed alkaline sulphides, and in the caustic alkalies. It is only sparingly soluble in cold concentrated nitric acid; but upon the application of heat, even when the acid is somewhat dilute, it readily dissolves, forming a blue solution of the nitrate, with more or less copper sulphate. It is slowly dissolved by hot concentrated hydrochloric acid, with the formation of the monochloride of copper; concentrated sulphuric acid has but little action upon it in the cold, but it is decomposed by the hot acid. In its dry state, sulphide of copper has a greenish-black color; when exposed to moist air, it slowly absorbs oxygen, and becomes converted into copper sulphate.

In examining the limit of this test, *ten grains* of the copper solution were submitted to a slow stream of the washed sulphuretted gas.

1. 1–100th solution of copper oxide ($=\frac{1}{10}$ grain CuO) yields an immediate deep brown precipitate, which soon becomes brown-

ish-black. After standing some time, the precipitate entirely separates as a copious, black deposit, leaving the solution perfectly colorless.

2. 1–1000th solution yields at first a brown mixture, from which, after a time, a brownish-black deposit separates, leaving the liquid of a brownish color. After standing some hours, the liquid becomes colorless, and the deposit acquires a greenish-black color.
3. 1–5000th solution: the solution immediately assumes a brown color, and soon becomes turbid; after several hours a quite fair greenish-black deposit separates.
4. 1–10,000th solution: the liquid immediately acquires a brownish color, which soon deepens; after the mixture has stood about twenty-four hours, it yields a greenish-brown deposit.
5. 1–25,000th solution: the liquid immediately assumes a yellow brown color, which soon changes to brown; in twenty-four hours a satisfactory light brown deposit has formed.
6. 1–50,000th solution: almost immediately the liquid assumes a yellowish color, and soon becomes brownish-yellow; in twenty-four hours quite perceptible brownish flakes have separated, and the liquid has a brownish color.
7. 1–100,000th solution: after several minutes the liquid acquires a faint yellowish color, which soon becomes quite distinct; in twenty-four hours it has a faint brownish hue, but there is no precipitate.

This reagent also produces brownish precipitates with several other metals, but most of these are extremely rare and not likely to be met with in medico-legal investigations. The transition of color observed in the sulphide of copper is somewhat peculiar to this substance, especially when the metal is present in quite notable quantity. When the sulphide is moistened with hydrochloric acid and touched for a little time with a bright sewing-needle, the latter becomes coated with metallic copper of its peculiar color. The true nature of the precipitate may also be established by dissolving it, by the aid of heat, in a little nitric acid, evaporating the solution to dryness, dissolving the residue in a little water, and testing the solution with ammonia or potassium ferrocyanide, in the manner described hereafter.

Neither nickel, chromium, uranium, nor cobalt—metals which,

like copper, have the property of forming green or blue salts—will yield a precipitate from *acid* or *neutral* solutions when treated with sulphuretted hydrogen gas.

2. *Ammonia.*

This reagent produces in solutions of salts of copper a blue or greenish-blue, amorphous precipitate, which is readily soluble, to a deep blue solution, in excess of the precipitant. With very dilute cupreous solutions the reagent may fail to produce a precipitate, but the liquid immediately assumes a blue color, which is readily destroyed upon the addition of a free acid.

1. $\frac{1}{100}$ grain of copper oxide, in one grain of fluid, yields a copious precipitate, which with excess of the reagent dissolves to an intensely blue solution.
2. $\frac{1}{1000}$ grain yields a blue, flocculent deposit, which readily dissolves in excess of the precipitant, forming a distinctly blue liquid.
3. $\frac{1}{5000}$ grain, with a very minute quantity of the reagent, yields a very distinct precipitate: this precipitate is best obtained by exposing the copper solution to the vapor of ammonia; when the precipitate is dissolved in excess of the reagent, the mixture has a just perceptible blue tint.
4. $\frac{1}{10,000}$ grain, when exposed to the vapor of ammonia, yields a distinct precipitate, which, when dissolved in excess of the precipitant, forms an apparently colorless liquid. *Ten grains* of the solution have a quite distinct blue color. This blue color is quite obvious in much more dilute solutions, when larger quantities of the liquid are examined.

Normal solutions of salts of nickel yield with ammonia a partial precipitate of green, hydrated oxide of nickel, which, like the copper precipitate, is readily soluble in excess of the reagent, forming a deep blue solution. Solutions of salts of cobalt yield with the reagent a blue precipitate, which dissolves in excess of the precipitant, forming a reddish-brown liquid. From solutions of the salts of sesquioxide of chromium, ammonia throws down a bluish-green precipitate, which is slightly soluble in excess of the reagent, with the formation of a pink solution. Salts of uranium yield with the reagent a yellow precipitate, which is insoluble in excess of the precipitant.

3. *Potassium and Sodium Hydrates.*

The fixed caustic alkalies throw down from solutions of salts of copper a blue amorphous precipitate of cupric hydrate, or hydrated oxide of copper, CuO,H_2O, which is insoluble in excess of the precipitant, but readily soluble in acids, even acetic acid. On boiling the mixture containing an excess of the reagent, the precipitate speedily becomes anhydrous and of a black color: this change is slowly effected even at ordinary temperatures.

The reaction of these reagents is much modified by the presence of certain organic substances. Thus, in a solution of the sulphate of copper containing *grape-sugar*, the precipitate is readily *soluble* in excess of the precipitant, forming a deep blue solution, from which the whole of the copper is thrown down by boiling, in the form of a *yellow* or *red* powder of cuprous oxide, or suboxide of copper, Cu_2O. In the presence of tartaric acid the reagent may fail to produce a precipitate, even upon boiling the mixture.

1. $\frac{1}{100}$ grain of copper oxide, in one grain of water, yields a copious, blue, gelatinous deposit.
2. $\frac{1}{1000}$ grain: a very good, flocculent precipitate.
3. $\frac{1}{5000}$ grain yields in a very little time a slight, flocculent precipitate, which soon becomes a quite fair deposit.
4. $\frac{1}{10,000}$ grain: after a little time a just perceptible cloudiness, and soon a quite distinct, flaky deposit.

These reagents also produce a blue precipitate in solutions of salts of cobalt, which is insoluble in excess of the reagent; but when this mixture is boiled, the precipitate is changed into a brownish or reddish deposit. Solutions of the sesquioxide of chromium yield with the reagent a bluish-green precipitate, readily *soluble* in excess of the precipitant, forming a greenish liquid, from which, by continued boiling, the whole of the chromium is reprecipitated as green, hydrated sesquioxide of the metal. These are the only two metals which yield with these reagents precipitates the color of which might be confounded with that of the copper precipitate.

Potassium and sodium carbonate occasion in aqueous solutions of cupreous salts a greenish-blue, amorphous precipitate of hydrated oxycarbonate of copper, $CuO,CuCO_3,H_2O$, which is sparingly soluble, to a bluish liquid, in excess of the precipitant. If an excess of the reagent be added and the mixture boiled, the precipitate

becomes converted into black anhydrous cupric oxide. The limit of the reaction of these reagents is the same as that of the fixed caustic alkalies.

4. *Potassium Ferrocyanide.*

This reagent throws down from somewhat strong solutions of salts of copper a reddish-brown, amorphous precipitate of ferrocyanide of copper, Cu_2FeCy_6, which is insoluble in excess of the precipitant, and in acetic and hydrochloric acids, but sparingly soluble in ammonia to a bluish-green liquid, from which it is reprecipitated by excess of acetic acid. From more dilute solutions the reagent produces a purple precipitate; while from still more dilute solutions it fails to produce a precipitate, but the mixture assumes a reddish color.

1. $\frac{1}{100}$ grain of copper oxide yields a copious, reddish-brown, gelatinous precipitate.
2. $\frac{1}{1000}$ grain: an immediate purple precipitate, which soon becomes a quite good, reddish-brown deposit.
3. $\frac{1}{10,000}$ grain: a reddish, flocculent turbidity.
4. $\frac{1}{25,000}$ grain yields a slight cloudiness; when viewed over white paper, the mixture exhibits a distinct reddish color.

When *five grains* of a 1–100,000th solution are treated with a small quantity of the reagent, the mixture presents a quite distinct reddish color. This color is readily observed even in more dilute solutions, when larger quantities are examined.

Potassium ferrocyanide also produces in solutions of uranic salts a precipitate very similar in color to that of the ferrocyanide of copper. But the uranium precipitate is changed to a *yellow* compound upon the addition of excess of ammonia; whereas, as before stated, the copper ferrocyanide is soluble to a limited extent in excess of this alkali, yielding a bluish-green liquid. Moreover, solutions of copper are readily distinguished from those of uranium by their behavior with sulphuretted hydrogen and ammonia, as already pointed out. Copper and uranium are the only metals that yield reddish-brown precipitates with potassium ferrocyanide.

The reaction of this reagent with solutions of salts of copper is much modified by the presence of even minute quantities of iron, with which it produces a blue precipitate.

5. *Iron Test.*

When a piece of bright iron or steel is immersed in a solution of a salt of copper, it sooner or later decomposes the salt and receives a coating of metallic copper, having the characteristic color of the metal; at the same time, a salt of iron, containing the acid previously combined with the copper, is formed. This reaction, especially from dilute solutions, is much facilitated by the presence of a little free sulphuric or hydrochloric acid.

In examining the limit of this test, a single grain of the copper solution, placed in a watch-glass, was acidulated with sulphuric acid, and a small portion of a bright sewing-needle introduced into the mixture; in the very dilute solutions the length of the needle did not exceed $\frac{1}{16}$ of an inch. It is obvious that the thickness of the deposit from a given quantity of copper, and consequently the delicacy of the test, will depend very much upon the extent of surface over which the metal is distributed.

1. $\frac{1}{100}$ grain of copper oxide yields a very fine coating.
2. $\frac{1}{1000}$ grain: in a little time the needle acquires a very satisfactory deposit.
3. $\frac{1}{10,000}$ grain: in a few minutes the needle presents a reddish tint, and in fifteen minutes receives a satisfactory coating.
4. $\frac{1}{20,000}$ grain: after several minutes the needle exhibits a just perceptible reddish hue, which improves, and after an hour becomes perfectly satisfactory.

By allowing the needle to remain in the acidulated liquid for several hours, satisfactory deposits may be obtained from solutions much more dilute than the last-mentioned. The true color of very thin deposits is best determined by the aid of a hand-lens.

It need hardly be remarked that this reaction is peculiar to copper. The cupreous nature of the deposit may be shown by dissolving out the iron from the coated needle with diluted sulphuric acid, and then dissolving the washed coating in a little nitric acid, evaporating the solution to dryness, redissolving the residue in a few drops of water, and testing the liquid with potassium ferrocyanide.

6. *Platinum and Zinc Test.*

When a solution of a salt of copper is acidulated with hydrochloric or sulphuric acid, and placed in a platinum dish, and then a

fragment of bright zinc placed in the liquid, the cupreous compound quickly undergoes decomposition, with the deposition of a coating of metallic copper, of its peculiar color, upon the platinum covered by the liquid.

1. $\frac{1}{100}$ grain of copper oxide in one grain of fluid, when treated after this method, yields a very fine deposit.
2. $\frac{1}{1000}$ grain: after a few minutes the platinum exhibits a very satisfactory coating.
3. $\frac{1}{5000}$ grain: after several minutes there is a quite distinct deposit.

This method will not serve for the detection of as minute quantities of copper as the iron test, since in its application the metal is distributed over a larger surface than when the iron-method is employed. If the washed deposit be moistened with a few drops of caustic ammonia, the liquid slowly acquires a blue color, due to the formation of a soluble compound of the metal.

7. *Potassium Arsenite.*

This reagent throws down from neutral solutions of salts of copper, when not too dilute, a bright green precipitate of cupric arsenite, $CuHAsO_3$, known also as Scheele's green. This precipitate is readily soluble in ammonia and in free acids.

1. $\frac{1}{100}$ grain of copper oxide, in one grain of water, yields a copious precipitate.
2. $\frac{1}{1000}$ grain: a quite good, yellowish-green deposit.
3. $\frac{1}{10,000}$ grain: after a little time the mixture becomes decidedly turbid; but the green color is not perceptible. With larger quantities of the solution the reagent produces satisfactory results, even in much more dilute solutions.

The production of a bright green precipitate by this reagent is quite characteristic of copper. However, solutions of salts of nickel yield with the reagent a pale green deposit, which, like the copper precipitate, is readily soluble in ammonia and in acetic acid.

8. *Potassium Chromate.*

Monochromate of potassium, when added in excess to somewhat strong solutions of salts of copper, produces a reddish-brown precipitate of cupric chromate, which is readily soluble in ammonia, forming a beautiful green liquid; the precipitate is also soluble in acetic acid, and in excess of the copper solution. From more dilute

solutions the reagent throws down a yellow or greenish-yellow deposit.

1. $\frac{1}{100}$ grain of copper oxide, in one grain of water, yields a very copious, reddish-brown, amorphous precipitate.
2. $\frac{1}{1000}$ grain: a copious, yellow deposit, which soon assumes a greenish-yellow color.
3. $\frac{1}{10,000}$ grain yields an immediate bluish-yellow turbidity, and soon a quite satisfactory greenish-yellow precipitate.
4. $\frac{1}{40,000}$ grain: after several minutes a quite perceptible turbidity.

Potassium dichromate fails to produce a precipitate, even in concentrated solutions of salts of copper.

9. *Potassium Ferricyanide.*

Normal solutions of salts of copper yield with this reagent a brownish-yellow or greenish-yellow amorphous precipitate of cupric ferricyanide, which is insoluble in acetic acid, but is readily soluble in ammonia, forming a beautiful green fluid.

1. $\frac{1}{100}$ grain of copper oxide yields a copious, brownish-yellow precipitate.
2. $\frac{1}{1000}$ grain: a very good deposit.
3. $\frac{1}{5000}$ grain: a rather good, greenish-yellow precipitate.
4. $\frac{1}{10,000}$ grain yields a greenish turbidity.

The production of a brownish or greenish-yellow precipitate by this reagent is common to solutions of several other metals besides copper.

10. *Potassium Iodide.*

This reagent produces in solutions of salts of copper a yellow or brownish-yellow precipitate, which soon changes to a brownish or yellowish-white deposit of cuprous iodide, Cu_2I_2; at the same time iodine is set free, and dissolves in any excess of the reagent present: $2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2$. The precipitate is insoluble in acetic acid, but is readily soluble to a deep blue solution in ammonia.

1. $\frac{1}{100}$ grain of copper oxide yields a copious, brownish-yellow precipitate, which soon acquires a yellowish-white color.
2. $\frac{1}{1000}$ grain: a quite good deposit.
3. $\frac{1}{5000}$ grain: the liquid assumes a yellow color, then becomes turbid, and after a short time throws down small granules.

4. $\frac{1}{10,000}$ grain: after a little time the mixture acquires a yellow color, then becomes turbid.

The production by this reagent of a brownish or yellowish precipitate, which is readily soluble in ammonia to a deep blue solution, is quite peculiar to solutions of copper.

Guaiacum Test.—If a solution of a salt of copper to which a little common salt has been added be poured gently down the side of a test-tube containing an alcoholic solution of guaiacum, a blue color is produced at the junction of the two liquids, even when only a minute trace of copper is present; and if in larger quantity, the whole liquid becomes blue on agitation. In this manner, according to E. Purgotti, who first observed the reaction (1878), 0.001 milligramme of copper sulphate will yield a blue coloration.

In applying this test it must be borne in mind that ferric compounds and certain other substances have also the property of bluing a like solution of guaiacum. These objections may, for the most part at least, be answered by first adding the copper solution to the guaiacum tincture, and then, if no color is developed, adding to the mixture a minute crystal of sodium chloride, when the crystal will become surrounded with a deep blue coloration, even if only a very minute quantity of the metal is present.

Detection of the Acid.—The tests now considered would, of course, serve only for the detection of the metal of the copper compound, and would not indicate the acid with which it was combined. The presence of sulphuric, hydrochloric, or nitric acid, when combined with the metal, could be shown in the manner already described under the special consideration of these acids.

The presence of acetic acid, as in the case of verdigris, could be shown by boiling the cupreous salt with a small quantity of a mixture of about equal volumes of strong sulphuric acid and alcohol, when acetic ether of its characteristic odor would be evolved.

Separation from Organic Mixtures.

Suspected Solutions.—The soluble salts of copper are more or less decomposed, with the precipitation of oxide of the metal in combination with organic matter, by various animal and vegetable principles. A portion of the clear liquid, after concentration, if

deemed best, may be slightly acidulated with sulphuric acid, and a portion of a bright-sewing needle placed in the mixture, the immersion being continued for several hours if necessary. Any metallic deposit thus obtained may be washed and confirmed by dissolving the needle in diluted sulphuric acid, and afterward the washed coating in nitric acid, in the manner already described when considering the iron test.

In the application of this test, it should be borne in mind that the needle may after a time, even in the absence of copper, present a reddish appearance, due to the formation of a coating of iron oxide. A deposit of this kind, however, may be readily distinguished from that produced by copper, even in most instances by examining it with a hand-lens. Should the iron test reveal the presence of copper, other portions of the liquid may be examined by some of the other tests for the metal. Most of these tests, however, have their action readily interfered with by the presence of organic matter.

Should the liquid presented for examination be mixed with much solid organic matter, the mixture, after the addition of water if necessary, may be gently heated for some time, and a portion of the filtered liquid then examined in the manner before described. Should there be a failure thus to detect the poison, there would be little doubt of its entire absence. Yet, the solids separated from the liquid by filtration may be boiled for about fifteen minutes with water containing a little hydrochloric acid, and the solution thus obtained be examined either by the iron test or by sulphuretted hydrogen gas.

Contents of the Stomach.—These are carefully transferred to a clean porcelain dish, and the inside of the stomach well scraped, the scrapings being added to the matters in the dish. The contents of the dish, after the addition of water if necessary, are strongly acidulated with hydrochloric acid, and gently boiled until the organic solids are well broken up. The cooled liquid is then filtered, the filtrate somewhat concentrated, again filtered, and then exposed to a slow stream of sulphuretted hydrogen gas, as long as a precipitate is produced, by which any copper present will be thrown down as sulphide of the metal. When the precipitate has completely subsided, it is collected on a filter, washed, and then dissolved, by the aid of heat, in a small quantity of diluted nitric acid. On now treating the solution with a drop or two of sulphuric acid and cautiously

evaporating it to dryness, the metal, if present, will be left as blue copper sulphate. The residue thus obtained is dissolved in a small quantity of warm water, and the filtered solution examined for copper by the ordinary reagents, especially by the iron and ammonia tests.

Should the precipitate produced by sulphuretted hydrogen be small in quantity and apparently contain much organic matter, the residue obtained after solution in nitric acid and evaporation is moistened with concentrated nitric acid and heated until the organic matter is entirely destroyed. The dry mass is then treated with a little diluted nitric acid, the liquid expelled by a moderate heat, the residue dissolved in a little pure water, and the solution tested.

From the Tissues.—For the purpose of examining any of the soft tissues of the body for absorbed copper, the organ, as a portion of the liver cut into small pieces, is made into a paste with pure nitric acid diluted with three or four volumes of water, and the mixture gently boiled, with the occasional addition of small quantities of powdered potassium chlorate, until the whole becomes perfectly homogeneous. It is then diluted with water, allowed to cool, and the filtered liquid evaporated to dryness. The residue thus obtained, placed in a thin porcelain capsule, is covered with concentrated nitric acid, a little potassium chlorate added, and the liquid evaporated by a moderate heat; the heat is then increased and continued until the organic matter is entirely destroyed, when the mass will assume a nearly white color. On boiling this residue in nitric acid containing a little water, any copper present, together with the small quantity of iron which is usually present in the tissues, will be taken up in a soluble form. This solution is carefully evaporated to dryness, to expel the excess of nitric acid, the residue dissolved in a little warm water, and tested in the usual manner. Should the solution contain iron, any copper present may be separated from that metal by acidulating the liquid with hydrochloric acid and treating it with sulphuretted hydrogen, when the copper will be thrown down as sulphide of the metal, while the iron will remain in a soluble form; the precipitated copper sulphide is then collected on a filter, washed, dissolved in a little nitric acid, and the solution examined in the manner already indicated.

Another method for the separation of iron, when present in a liquid with copper, is to treat the solution with excess of ammonia,

when the former metal will be precipitated as hydrated sesquioxide of iron, while the copper will remain in solution, forming a deep blue liquid. After removing the iron precipitate by a filter, a portion of the filtrate may be slightly acidulated with acetic acid, and tested with a solution of potassium ferrocyanide.

In a case of poisoning by copper sulphate, M. Malagutti readily detected the metal in a portion of the liver of the deceased; and also in about two ounces of the urine. (*Jour. de Chim. Méd.*, April, 1862, 209.)

In an instance in which two women had suffered with symptoms resembling those produced by copper compounds, and almost incessant vomiting for two or three weeks, the bodies when exhumed several months after death were found in a remarkable state of preservation, and the liver in each case contained 0.120 gramme (1.85 grains) and 0.080 gramme (1.23 grains) respectively of copper. (*Ibid.*, 1874, 504.)

In experiments on animals, in regard to the elimination of the salts of copper, I. L. Orfila administered small quantities of the sulphate, mixed with food, to dogs for fifteen days, and found the metal in the liver, in the tissue of the stomach, and in the lungs sixty days after it had been administered. But the metal was found in the urine for only a few days after it had ceased to be taken; and even in some instances it was not detected after the lapse of twenty-four hours. (*Orfila's Toxicologie*, i. 791.)

MM. Bournville and Yvon relate the case of an epileptic patient who was given, during a period of four months, forty-three grammes (six hundred and fifty grains) of the ammonio-sulphate of copper. The medicine was then discontinued, and at the end of three months the patient died from tuberculosis. On inspection, the stomach and intestines presented no appearance which could be attributed to the copper compound, but the liver contained 0.295 gramme (four and one-half grains) of metallic copper, corresponding to 1.166 gramme of crystallized sulphate of the metal. (*Jour. de Chim. Méd.*, May, 1875, 236.)

From the Urine.—About five ounces or more of the urine are evaporated to dryness, and the organic matter of the residue destroyed by means of concentrated nitric acid and potassium chlorate, and subsequent incineration. The ash thus obtained, which will generally contain a small trace of iron, is dissolved in hot diluted nitric

acid, and the liquid evaporated. Any nitrate of copper present in the residue is then dissolved in a small quantity of water, and the solution examined in the usual manner.

In six cases of non-fatal poisoning by salts of copper, collected by M. Kletzinsky, the metal was found in the urine as long as the patients experienced any active symptoms. When these ceased, the metal disappeared from the urine; but it continued to be discharged with the fæces. (Thudichum, *Pathology of the Urine*, 409.)

Quantitative Analysis.—Copper is usually estimated as cupric oxide, or monoxide of the metal. The solution is heated to about the boiling temperature, and a solution of potassium or sodium hydrate added as long as a precipitate is produced, after which the heat is continued for some minutes. When the mixture has cooled and the supernatant liquid become perfectly clear, the precipitate is collected on a filter of known ash, washed with warm water, and dried. It is then, as far as practicable, separated from the filter, strongly ignited in an equipoised platinum capsule, and the ash of the filter, which has been burned separately, added to the ignited mass; the whole is then allowed to cool, and quickly weighed. When the quantity of precipitate is small, it may be ignited along with the filter.

Should the alkaline liquid separated by filtration from the precipitated oxide of copper have a blue color, it is boiled with a little grape-sugar, when any copper still present will be thrown down as suboxide of the metal; this is collected, washed, moistened with nitric acid, the liquid evaporated, and the residue ignited, when the copper will remain as cupric oxide. One hundred parts by weight of anhydrous monoxide of copper correspond to 314.21 parts of pure crystallized sulphate of copper.

Section III.—Zinc.

History and Chemical Nature.—The symbol for zinc is Zn, its atomic weight 65.2, and its specific gravity about 7. Zinc is found in nature under several forms of combination, but chiefly as carbonate of the metal. Zinc is a bluish-white metal having a bright metallic lustre, very brittle, and, when fractured, exhibits a crystalline structure. It fuses, according to Daniell, at 412° C. (773° F.),

and at a red heat is volatilized, being dissipated in the form of a colorless vapor, which, in the presence of air, takes fire and burns with a white flame, forming oxide of zinc, ZnO. When heated on a charcoal support before the reducing blow-pipe flame, it fuses, then burns, evolving dense white fumes, and coating the charcoal with a yellow incrustation, which on cooling becomes white.

Exposed to the air, at ordinary temperatures, zinc becomes covered with a gray coating of basic carbonate of zinc. The metal is readily dissolved by nitric acid, with the formation of zinc nitrate, and the evolution of either suboxide or monoxide of nitrogen, the nature of the evolved gas depending upon the strength of the acid employed. It is also readily soluble in diluted sulphuric and hydrochloric acids, with the formation of a salt of zinc and the evolution of hydrogen gas. As found in commerce, metallic zinc is liable to be contaminated with carbon, arsenic, sulphur, antimony, iron, lead, and cadmium.

Zinc unites with oxygen in only one proportion, forming the monoxide. This forms a white, amorphous powder, which at elevated temperatures has a lemon-yellow color. The *salts* of zinc, unless they contain a colored acid, are colorless. They are for the most part readily soluble in water, and their normal solutions have a slightly acid reaction. When intimately mixed with sodium carbonate, and heated before the blow-pipe on a charcoal support, the salts of zinc are readily decomposed, with the formation of an incrustation, over the charcoal, of oxide of zinc.

When taken into the stomach, metallic zinc is destitute of poisonous properties, at least so long as it retains its metallic state; but all the preparations of this metal are more or less poisonous; they are, however, less active than the compounds of lead and copper. The continued inhalation of the oxide of zinc has, in several instances, given rise to serious symptoms. (*Chem. Gaz.*, viii. 362; also *Med.-Chir. Rev.*, July, 1873, 254.) MM. Lechartier and Bellamy state that they found minute traces of zinc in the livers of various men of different occupations and who had died of different diseases; in the muscles of an ox, in the liver of a calf, and in the eggs of the common fowl; also in wheat, maize, barley, and beet-root. (*Chem. News*, May, 1877, 182.)

The only salts of zinc requiring notice in this connection are the sulphate and chloride. Poisoning by these salts has been of rare occurrence, and has been chiefly the result of accident.

Sulphate of zinc, or *white vitriol*, $ZnSO_4,H_2O,6Aq$, as usually found in the shops, is in the form of small, colorless, prismatic crystals, which have a strongly astringent, metallic taste, and are slightly efflorescent in dry air. At 100° C. (212° F.) the crystallized salt gives up six molecules of water, and at about 204° C. (400° F.) becomes anhydrous; at a bright red heat it is entirely decomposed, leaving a residue of zinc oxide. It is soluble in about two and a half times its weight of water at ordinary temperatures; and in less than its own weight of boiling water. It is insoluble in alcohol, ether, and chloroform.

Chloride of zinc, $ZnCl_2$, is readily obtained by dissolving zinc in diluted hydrochloric acid, and evaporating the solution to dryness. In its anhydrous state it forms a soft, white, very deliquescent solid, which is readily fusible, and volatilizes unchanged at a strong red heat, condensing sometimes in the form of colorless, crystalline needles. It is soluble in water in all proportions, and also soluble in alcohol and ether. The liquid known in the shops under the name of "Sir Wm. Burnett's disinfecting fluid" is a solution of this salt, containing about two hundred grains of the anhydrous salt in each fluid-ounce. Several instances of poisoning by this liquid have been reported.

Symptoms.—Sulphate of zinc has frequently been administered in doses of several grains daily for long periods without producing any ill effects. Dr. Babington even gave, in one instance, thirty-six grains of the salt, three times a day for three weeks, without any noxious symptom having appeared. When, however, the salt is swallowed in doses of several drachms or more, it may produce very speedy and violent symptoms, and even death. The usual symptoms are an astringent taste in the mouth, a sense of constriction and burning in the throat and fauces, nausea, violent vomiting, intense pain in the stomach and bowels, frequent purging, small and frequent pulse, great anxiety, and coldness of the extremities. The intellect usually remains clear.

A robust woman, aged twenty-five years, swallowed, by mistake for Epsom salt, a solution containing an ounce and a half of zinc sulphate. She instantly vomited, and then became affected with almost incessant retching and purging for half an hour, which continued afterward, at short intervals, for three hours. There was also a small and frequent pulse, extreme prostration, great anxiety, cold-

ness of the body, violent pain in the abdomen and limbs, with a sense of burning in the throat and stomach, and death ensued in thirteen hours and a half after the poison had been taken. A sister of this woman, aged thirty-five years, took at the same time a similar dose of the poison, but after several days of severe illness she finally recovered. In this instance the vomiting was delayed for fifteen minutes, and there was no purging for ten hours; the other symptoms much resembled those of her sister, except the burning sensation in the throat, which was absent. (*Amer. Jour. Med. Sci.*, July, 1849, 279; from *Brit. and For. Med.-Chir. Rev.*, April, 1849.)

A case of slow poisoning by the sulphates of zinc and iron has been reported by Dr. Wm. Herapath. (*Chem. News*, June, 1865, 288.) The symptoms were a sense of burning heat in the stomach, fauces, and gullet, coppery taste in the mouth, great thirst and nausea after eating and drinking, followed by vomiting after from half an hour to an hour. After death, the stomach was found considerably inflamed in the cardiac portion, and its inner surface was in a blistered state; the intestines were but slightly inflamed. Traces of zinc and iron sulphates were found in the vomited matters, and also in the contents of the lower intestines; but in the contents of the stomach and duodenum only sulphate of iron was found.

The following case of recovery is reported by Dr. J. W. Ramsey. (*Med. and Surg. Rep.*, Feb. 1869, 178.) A woman in ordinary health, aged twenty-eight, took in mistake for Epsom salt a large tablespoonful of zinc sulphate. Violent vomiting, with cramps, severe burning pain in the stomach, and extreme prostration, soon ensued. An hour later, the pulse was very feeble, small, and easily compressible, the respiration difficult; there was violent coughing, a copious flow of tears from the eyes, and constant desire to discharge the fæces. Under treatment the patient was soon convalescent, but experienced difficulty of breathing, great prostration, and intense itching with a sense of burning in the skin, especially during the night, for several days afterward. In a case reported by Dr. Brennan, a man recovered after having taken by mistake *four ounces* of this salt.

In poisoning by solutions of the *chloride of zinc*, the symptoms are much the same as those caused by the sulphate. There is an immediate burning sensation in the throat, burning pain in the stomach, nausea, violent vomiting, purging, cold perspirations, great anxiety, and feeble pulse. In some instances the vomited matters

are streaked with blood, owing to the local action of the poison upon the throat and neighboring parts.

In a case of poisoning by Burnett's disinfecting fluid, reported by Dr. Letheby, the patient, a child fifteen months old, was seized with extreme prostration, and died in a comatose condition, *ten hours* after taking the dose. In a case communicated to Dr. Taylor, a woman, aged twenty-eight years, swallowed an ounce of this fluid, and died from its effects *four hours* afterward. This is perhaps the most rapidly fatal case of poisoning by zinc yet recorded. A woman, forty years of age, swallowed a quantity of Burnett's fluid in mistake for a glass of gin. It remained on the stomach only about ten minutes, when it was ejected by vomiting. A burning sensation was experienced in the throat and chest for two or three days; this was succeeded by an inability of the stomach to retain food, and death ensued at the expiration of fourteen weeks, apparently from simple prostration, due to want of nourishment. (*Amer. Jour. Med. Sci.*, Jan. 1860, 190.) In an instance reported by Dr. Stratton, of Montreal, a man, aged fifty-four years, drank about a wineglassful of a dense solution of chloride of zinc, containing, as prepared, four hundred grains of the salt, and entirely recovered from its effects; not, however, without experiencing very severe symptoms for several days.

As *metallic zinc* is more or less acted upon by certain articles of food, especially such as contain free organic acids or fatty matters, its use for culinary operations is not altogether free from danger. In an instance in which we were consulted, a family, consisting of eight persons, suffered with symptoms of zinc poisoning, occasioned by the use of apple-butter prepared with cider which had been concentrated on a *galvanized* iron pan. On chemical examination, the concentrated cider was found to contain 1.14 grains of zinc oxide in each fluid-ounce.

P. van Hamel-Roos reports an instance (*Chem. News*, May, 1879, 237) in which seven persons were poisoned by using in the preparation of food *enamelled* iron pans containing oxide of zinc. The oxide was readily dissolved from the enamel by heating with highly diluted acetic acid and common salt.

Even ordinary *water* when kept in contact with zinc will, after a time, act upon the metal and dissolve it in notable quantity. This action is less likely to take place with hard waters than with rain-water.

Treatment.—This is much the same as in poisoning by salts of lead and copper. No chemical antidote is known. The efforts of the stomach should be assisted by the free administration of mild demulcent drinks. The free exhibition of a mixture of milk and magnesium hydrate, and also of decoctions of the vegetable astringents, has been recommended. In poisoning by the chloride of zinc, a solution of acid sodium carbonate, followed by large draughts of any bland liquid, has been advised. Opium may be found useful to allay the subsequent irritation.

Post-mortem Appearances.—In the case already cited, in which an ounce and a half of the sulphate of zinc proved fatal in thirteen hours and a half, the following appearances were observed, forty hours after death: great lividity of the external surface of the body; congestion of the brain and its membranes; a congested state of the lungs; flaccid condition of the heart, the right cavities being filled with black, thick blood; the inner surface of the stomach was covered with a yellowish, pultaceous matter, on the removal of which a uniform yellow, ochreous color was observed, except towards the great curvature, where it became reddish; there was also a gelatiniform softening of the mucous membrane of the stomach, exposing, in some parts, the submucous cellular tissue. The small intestines were somewhat injected, and contained yellowish matters. In another case the stomach was very vascular, spots of ecchymosis being observable, and near the pylorus slight ulceration. The brain and its membranes were much congested, and the pleura contained a large quantity of sanguinolent fluid. (*Amer. Jour. Med. Sci.*, July, 1849, 280.)

In a case reported by Dr. Ogle, in which the poison seems to have been taken, with suicidal intent, in frequent doses for a week prior to death, the mucous surface from the mouth to the stomach was slightly congested, and its surface thickened in patches, and of a grayish-white color. The stomach was contracted, and the whole of its inner surface was of a dirty-gray color, the mucous membrane being very greatly thickened, condensed, and indurated, and having an appearance similar to that of tripe. The duodenum had the same appearance in a less degree; the colon and rectum were contracted, but otherwise healthy. There was general congestion of the visceral organs, and a dark, fluid condition of the blood. (*Lancet*, 1859, ii. 210.)

In a case quoted by Dr. A. Stillé (*Mat. Med.*, ii. 336), which proved fatal on the fifth day, after a wineglassful of a concentrated solution of sulphate of zinc had been taken, the only morbid appearances detected were patches of inflammation of the mucous membrane of the pyloric end of the stomach and of the duodenum.

In Dr. Letheby's case of poisoning by *Burnett's disinfecting fluid*, before cited, twenty-two hours after death, the mucous membrane of the mouth, fauces, and œsophagus was found of a white color and opaque. The stomach was hard and leathery, and contained about an ounce and a half of liquid resembling curds and whey, in which chloride of zinc was afterward found. The inner surface of the stomach had a highly acid reaction, was corrugated, opaque, and tinged of a dark leaden hue; this appearance ceased abruptly at the pylorus. The lungs and kidneys were congested. In the case of poisoning by this fluid in which death did not occur until the lapse of fourteen weeks, the stomach was found so much contracted as to contain only four ounces of fluid, and completely perforated in two places by ulcers, one being near the cardiac and the other near the pyloric orifice. There was no decided peritonitis, but the whole of the serous membrane had a slightly greasy feel when touched, as if there was some exudation on its surface.

Chemical Properties.

In the Solid State.—When a few crystals of zinc sulphate, placed in a watch-glass, are treated with a drop of a solution of potassium chromate, they acquire a yellow color, and soon become converted into a mass of small yellow granules. This reaction, although perhaps not entirely peculiar, readily serves to distinguish the least visible crystal of the zinc salt from magnesium sulphate, or Epsom salt, for which it has in several instances been fatally mistaken, and which, when treated in a similar manner, slowly dissolves.

If a small portion of zinc sulphate be heated on a charcoal support in the inner blow-pipe flame, it quickly fuses in its water of crystallization, and leaves a residue which is slowly consumed, covering the charcoal in part with a yellow incrustation of zinc oxide, which on cooling becomes white. If the unconsumed residue, or the incrustation, be moistened with a solution of cobalt nitrate, and then heated in the outer flame of the blow-pipe, the mass on cooling acquires a *green* color. These reactions are peculiar to compounds

of zinc, and will serve for the identification of very minute quantities of the metal. It is usually best, however, before applying the blow-pipe heat, to mix the zinc compound with sodium carbonate.

Of Solutions of Zinc.—Pure aqueous solutions of zinc sulphate are colorless, have a styptic metallic taste, and slightly redden litmus-paper. When a drop of the solution is allowed to evaporate spontaneously, the salt is left in the form of slender prismatic crystals. As found in the shops, zinc sulphate is usually contaminated with iron, and sometimes contains other impurities, which more or less modify its chemical reactions.

In ascertaining the limit of the reactions of the different reagents for zinc, pure aqueous solutions of the sulphate were employed. The fractions indicate the fractional part of a grain of *oxide of zinc*, ZnO, or its equivalent, present in one grain of the solution. The results, unless otherwise stated, refer to the behavior of *one grain* of the solution. One part of the oxide corresponds to 3.54 parts of pure crystallized sulphate of zinc.

1. *Sulphuretted Hydrogen.*

Sulphuretted hydrogen gas throws down from neutral and alkaline solutions of salts of zinc a white amorphous precipitate of hydrated zinc sulphide, ZnS,H_2O, which is insoluble in the caustic alkalies, alkaline sulphides, and in acetic acid, but very readily soluble in the stronger mineral acids. In solutions containing either free sulphuric, hydrochloric, or nitric acid, the reagent fails to produce a precipitate. Even in strong solutions of the normal salts of these acids the reagent throws down only a portion of the zinc; but from solutions containing only about one per cent. or less of these salts the precipitation is complete. The separation of the precipitate, especially from very dilute solutions, is much facilitated by the application of a gentle heat.

The following results refer to the behavior of *ten grains* of a normal solution of zinc sulphate.

1. 1–100th solution of zinc oxide ($=\frac{1}{10}$ grain ZnO) yields an immediate precipitate, and soon there is a copious, white deposit.
2. 1–1000th solution: a quite good precipitate.
3. 1–10,000th solution: in a very little time the liquid becomes turbid, and after standing a few hours yields a very satisfactory deposit.

4. 1–25,000th solution: after a little time the mixture becomes turbid, and after a few hours there is a quite distinct deposit.
5. 1–50,000th solution: after a little time the liquid becomes cloudy, and after about ten hours a distinct, flaky deposit has formed.

The production of a white precipitate by this reagent is characteristic of zinc, as this is the only metal the sulphide of which has a white color. It should be remembered that the color of the precipitate may be much modified by the presence of even minute quantities of other metals. It must also be borne in mind that solutions of ferric salts may yield with sulphuretted hydrogen a white turbidity, due to the decomposition of the reagent with the separation of sulphur.

Ammonium sulphide produces the same precipitate of *zinc sulphide* from neutral and alkaline solutions of salts of the metal. In this case the precipitation is complete, even from concentrated normal solutions of any of the salts of the metal. This reagent, however, also produces in solutions of aluminium a white precipitate of *aluminium hydrated sesquioxide*, with evolution of sulphuretted hydrogen gas. This precipitate is easily distinguished from zinc sulphide, in being readily soluble in potassium hydrate.

2. *Potassium Hydrate and Ammonia.*

The fixed caustic alkalies and ammonia throw down from normal solutions of salts of zinc, and also from acid solutions when excess of the reagent is added, a white precipitate of *zinc hydroxide*, or hydrated oxide of zinc, ZnO,H_2O, which is readily soluble in free acids, and in excess of the precipitant. From these alkaline solutions the whole of the zinc is reprecipitated, as sulphide, by sulphuretted hydrogen gas.

1. $\frac{1}{100}$ grain of zinc oxide, in one grain of water, yields a copious, gelatinous precipitate.
2. $\frac{1}{1000}$ grain: a quite good, flocculent precipitate, which readily disappears on the addition of slight excess of the reagent.
3. $\frac{1}{10,000}$ grain yields with a very minute quantity of the reagent a slight turbidity.

These reagents also produce white precipitates in solutions of various other substances besides zinc; but from these precipitates the washed and dried zinc compound is readily distinguished by its behavior under the blow-pipe flame, as already pointed out.

The *alkaline carbonates* throw down from solutions of salts of zinc a white precipitate of a basic oxycarbonate of the metal, which is insoluble in excess of the fixed alkaline carbonates, but soluble in excess of the carbonate and other salts of ammonium. The precipitate is also readily soluble in acids, even acetic acid, and in the caustic alkalies. The limit of the reaction of these reagents is the same as that of the free alkalies.

3. *Potassium Ferrocyanide.*

This reagent produces in solutions of salts of zinc a white, amorphous precipitate of hydrated *zinc ferrocyanide*, $Zn_2Cy_6Fe,3H_2O$, which is insoluble in acetic, nitric, sulphuric, and hydrochloric acids; also in ammonia, in ammonium chloride, and in excess of the precipitant. In the presence of excess of the precipitant the precipitate acquires a greenish or greenish-blue color when acted upon by hydrochloric or nitric acid, due to the decomposition of the reagent. Ferrocyanide of zinc is readily soluble in potassium hydrate to a colorless solution, from which it is reprecipitated by an excess of hydrochloric acid.

1. $\frac{1}{100}$ grain of zinc oxide, in one grain of water, yields a very copious, gelatinous precipitate.
2. $\frac{1}{1000}$ grain: a quite good, flocculent deposit.
3. $\frac{1}{10,000}$ grain: in a very little time the mixture becomes quite turbid.
4. $\frac{1}{25,000}$ grain: after a few minutes a very perceptible turbidity.

This reagent also produces white precipitates in solutions of several other metals. Most of these precipitates, however, unlike that from zinc, are readily soluble in hydrochloric acid.

4. *Potassium Ferricyanide.*

This reagent occasions in solutions of salts of zinc a yellow, reddish-brown, or greenish, amorphous precipitate, the color depending upon the strength of the solution, and also, somewhat, upon the relative quantity of the reagent present. The precipitate is insoluble in acetic, hydrochloric, sulphuric, and nitric acids, but is readily soluble to a clear solution in potassium hydrate, from which it is reprecipitated by hydrochloric and sulphuric acids. It is also soluble in ammonia, but in a very little time the solution becomes turbid; from this solution it is also reprecipitated by acids.

1. $\frac{1}{100}$ grain of zinc oxide yields a copious, dirty-yellow precipitate, which very soon assumes a brownish color.
2. $\frac{1}{1000}$ grain: a good, greenish-yellow deposit.
3. $\frac{1}{10}\frac{1}{000}$ grain: a very fair, greenish turbidity, and very soon a flocculent precipitate.
4. $\frac{1}{25,000}$ grain: the mixture very soon becomes turbid, and in a little time yields perceptible flakes.

The reaction of this reagent is common to solutions of several different metals.

5. *Oxalic Acid.*

Oxalic acid throws down from solutions of salts of zinc a white, granular or crystalline precipitate of zinc oxalate, $ZnC_2O_4,2Aq$, which is insoluble in acetic acid, but readily soluble in the stronger mineral acids; it is also soluble in caustic ammonia, but almost insoluble in ammonium chloride. The separation of the precipitate is much facilitated by a gentle heat; also by agitation of the mixture.

1. $\frac{1}{100}$ grain of zinc oxide, in one grain of water, yields an immediate turbidity, and in a little time a copious granular precipitate.
2. $\frac{1}{1000}$ grain: in a little time a distinct precipitate, and soon a quite good deposit of granules and octahedral crystals, Plate V., fig. 6.
3. $\frac{1}{5000}$ grain: after several minutes small granules form along the margin of the drop, and in ten or fifteen minutes there is a very satisfactory granular and octahedral deposit.

Oxalic acid throws down white precipitates from solutions of salts of most of the metals, and in the case of calcium, and also of strontium, the precipitate may have the same microscopic characters as the oxalate of zinc. The true nature of the zinc precipitate, however, may be readily determined by its behavior before the blow-pipe.

6. *Potassium Chromate.*

Normal potassium chromate produces in solutions of zinc sulphate a bright yellow, amorphous precipitate, which, according to Thomson, consists of the subchromate of zinc. At ordinary temperatures the precipitate is somewhat slow to form, even from strong solutions, but it separates immediately on the application of heat.

It is insoluble in excess of the precipitant, but readily soluble in acetic acid, and in ammonia.

1. $\frac{1}{100}$ grain of zinc oxide yields, in the cold, an immediate cloudiness, and soon a copious, yellow precipitate.
2. $\frac{1}{1000}$ grain: an immediate turbidity, and soon a good, flocculent deposit.
3. $\frac{1}{10,000}$ grain: after a little time the mixture becomes quite turbid.

This reagent produces similar yellow precipitates in solutions of several other metals.

Potassium dichromate fails to produce a precipitate, even in concentrated normal solutions of salts of zinc.

7. *Sodium Phosphate.*

Ordinary sodium phosphate throws down from solutions of salts of zinc a white precipitate of tribasic zinc phosphate, Zn_32PO_4, which is soluble in acids, even in acetic acid, also in caustic potash and in ammonia, but only sparingly soluble in ammonium chloride. From strong solutions the precipitate as first produced is gelatinous, whilst from dilute solutions it is flocculent; but after standing some time it diminishes in volume and becomes converted, at least partially, into crystalline plates: this change is produced immediately or in a very little time by boiling the mixture.

1. $\frac{1}{100}$ grain of zinc oxide yields a quite copious gelatinous precipitate.
2. $\frac{1}{1000}$ grain: a good, flocculent deposit.
3. $\frac{1}{10,000}$ grain: after some minutes a quite distinct turbidity.

The production of a white precipitate by this reagent is common to solutions of quite a number of the metals.

Detection of the Acid.—The tests now considered would, of course, serve only for the detection of the base of the zinc salt. The presence of *sulphuric acid*, when combined with the metal, may be readily detected by acidulating the solution with nitric acid and treating it with barium chloride, by which the sulphuric acid will be precipitated as white barium sulphate, which is insoluble in nitric acid. The presence of *chlorine* or *hydrochloric acid* may be determined by treating the solution, acidulated with nitric acid, with silver nitrate, when any chlorine present will be thrown down as silver

chloride, which is readily soluble in ammonia, but insoluble in diluted nitric acid.

Separation from Organic Mixtures.

Contents of the Stomach.—The same method of analysis is equally applicable for the examination of suspected articles of food, vomited matters, and the contents of the stomach. Salts of zinc are more or less decomposed and precipitated by albumen, fibrin, casein, and certain other organic principles. When, therefore, the suspected mixture contains any solid matter, the whole, after the addition of water if thought best, should be acidulated with acetic acid and gently heated for some time, when any organic precipitate of zinc present will be dissolved. The solution thus obtained is filtered, and the filtrate, after concentration if necessary, treated with ammonium sulphide as long as a precipitate is produced, after which it is gently warmed, to facilitate the complete separation of the precipitate. The precipitate is then collected on a filter, washed, and while still moist digested with nitric acid, in which the zinc will dissolve, forming nitrate of the metal; at the same time, any iron present will be oxidized and dissolved as ferric nitrate. The solution is now evaporated to dryness, to expel the excess of acid, the residue dissolved in a small quantity of distilled water, and the filtered liquid examined by the ordinary tests for zinc.

Should the solution contain iron, which is a frequent impurity in salts of zinc, the chemical reactions of the latter, as already pointed out, will be more or less modified. These metals may be separated by the addition of *excess* of caustic ammonia, which will precipitate the iron as hydrated sesquioxide, while the zinc will be redissolved and remain in solution. Should the iron exist as a ferrous salt, before precipitating with ammonia it must be converted into a ferric salt, by boiling the mixture with a little nitric acid. After separating the precipitated iron oxide by a filter, the zinc in the ammoniacal filtrate may be precipitated as sulphide by sulphuretted hydrogen; or, the solution may be exactly neutralized with acetic acid, and then tested in the ordinary manner. As this neutralization would give rise to an ammonium salt, in which the precipitates produced by many of the reagents for zinc are more or less soluble, if only a minute quantity of the metal be present, it is best to expel the excess of ammonia, by evaporating the solution to dryness, and then redis-

solve the residue in a small quantity of water containing a drop or two of acetic acid.

From the Tissues.—Absorbed zinc may be recovered by boiling the finely divided tissue with nitric acid diluted with five or six volumes of water, until the organic matter is completely disintegrated. The mass is then transferred to a muslin strainer, the strained liquid evaporated to dryness, and the residue moistened with pure nitric acid, and heated until the organic matter is entirely charred. The dry mass thus obtained is treated with water containing a little hydrochloric acid, the filtered liquid evaporated to dryness on a water-bath, the residue dissolved in pure water, and the solution treated with ammonium sulphide. Any precipitate thus obtained is collected, washed, and examined in the manner before described.

In several instances of poisoning by the salts of zinc, the metal was readily discovered in the blood and tissues after death, even in some cases after comparatively long periods. It need hardly be remarked that when the metal is found in its absorbed state it will be impossible from chemistry alone to determine in what form it was originally taken.

Quantitative Analysis.—Zinc is usually estimated in the form of oxide of the metal. For this purpose the solution is heated to about the boiling temperature, and treated with a somewhat dilute solution of sodium carbonate as long as a precipitate is produced, after which it is boiled for some minutes. The precipitate is then allowed to subside, collected on a filter, washed with hot water, dried, and ignited. The whole of the zinc will now exist in the form of monoxide, one hundred parts of which correspond to 354.13 parts of pure crystallized sulphate, or 167.77 parts of anhydrous chloride of zinc.

PART SECOND.

VEGETABLE POISONS.

VEGETABLE POISONS.

INTRODUCTION.

NATURE OF VEGETABLE POISONS—GENERAL METHODS FOR RECOVERING THE ALKALOIDS FROM ORGANIC MIXTURES.

THE different poisonous plants owe their toxic properties to the presence of one or more proximate principles, some of which have not as yet been obtained in their isolated state. Most of these active principles have basic properties, and such, as a class, from their general chemical resemblance to the ordinary alkalies, have been named ALKALOIDS, or VEGETABLE ALKALIES. A few others, in regard to their chemical nature, are neutral; while others still have acid properties. In poisoning by these substances, the poison is usually taken in its more or less crude state; but in some instances, as in the case of strychnine and morphine, it is frequently taken in its pure form. The present consideration of this class of poisons will be confined to such as contain principles the nature of which, even when present only in minute quantity, can be fully established.

The natural *alkaloids* always exist in the plants from which they are obtained in the form of salts, which generally contain an organic acid peculiar to the plant in which the base is found. They all contain nitrogen, usually in the proportion of one atom, but sometimes two atoms, combined with various proportions of carbon and hydrogen, sometimes alone, but generally with the addition of oxygen. They are naturally divided into two classes: the *volatile* or *liquid*, and the *fixed* alkaloids.

The *volatile* alkaloids consist of carbon, hydrogen, and nitrogen; are liquid at ordinary temperatures; have a strong and peculiar odor; and pass over with the vapor of water when their free aqueous solu-

tions are distilled. On the other hand, the *fixed* alkaloids contain carbon, hydrogen, nitrogen, and oxygen; are solid at ordinary temperatures; destitute of odor; and do not distil with the vapor of water. In their free state most of the alkaloids are but sparingly soluble in water, but readily soluble in alcohol, ether, and chloroform. Their *salts* are, for the most part, soluble in water and in alcohol, but insoluble in ether and in chloroform.

In their *pure* state many of these substances may be identified with as much certainty, and in as minute quantity, as most of the inorganic poisons; but their detection when present in complex mixtures is generally much more difficult, requiring more care and delicacy of manipulation, and is attended with much greater loss of material than the recovery of inorganic substances. Again, as the quantity of the alkaloids necessary to prove fatal is usually very much less than that of inorganic poisons, the actual quantity of poison present in death from the former is generally much less than that in poisoning by the latter. Moreover, since all organic poisons sooner or later undergo complete decomposition in the dead body, they can at most be detected after only very limited periods, at least in comparison with some of the metallic poisons.

From these considerations it is obvious that in poisoning by these substances it may often happen that there will be a failure to detect the poison. Even when the poison is discovered, the amount recovered is frequently so minute as to render it impossible to make a quantitative analysis. In many instances the nearest approach that can be made as to the quantity recovered is by observing the intensity of the reactions of the reagents applied, and comparing these with the reactions of known quantities of the poison.

For the recovery and purification of the alkaloids, when mixed with foreign organic matters, several general methods have been proposed; but, as might be expected, these processes are not equally applicable for all the members of this class of poisons. Some of these methods—most of which are based upon the principles first pointed out in 1851 by M. Stas, of Brussels—will now be described, with some comments on each.

1. Method of Stas.

This method is much the same as that usually employed for extracting the alkaloids from the vegetables in which they occur. It

takes advantage of the fact that the acid salts of the alkaloids are soluble in water and in alcohol; and that when a solution of this kind is decomposed by the addition of an excess of a fixed mineral alkali or its carbonate and agitated with pure ETHER, this liquid will dissolve the liberated alkaloid. In the case of the volatile alkaloids, advantage is also taken of the insolubility of their acid salts in ether to separate such organic impurities as are soluble in this liquid, by agitating the mixture with the fluid while the alkaloid is in the form of a salt.

To apply this method, the suspected mixture, such as the contents of the stomach, is treated with about twice its weight of pure concentrated alcohol, then distinctly acidulated with tartaric or oxalic acid, and the whole heated in a flask to about 71° C. (160° F.). If the substance under examination is one of the solid organs of the body, as the liver, heart, or lungs, it is first cut into very small fragments and the mass moistened with strong alcohol, then strongly pressed, and the operation repeated with fresh portions of alcohol until the soluble matters are entirely extracted; the mixed alcoholic fluids are then acidified with tartaric or oxalic acid, and heated in the manner just described.

When the alcoholic mixture has entirely cooled, the fluid is filtered, the solids on the filter well washed with strong alcohol, and the mixed filtrates evaporated to near dryness at a temperature not exceeding 35° C. (95° F.), either in a strong current of air or in vacuo over sulphuric acid. If, during the evaporation, fatty or other insoluble matters separate, the concentrated fluid is filtered, the filter washed with alcohol, and the filtrate and washings evaporated as above, at a temperature not exceeding 35° C. The residue is then digested with cold absolute alcohol, the mixture filtered, the filter washed with alcohol, and the mixed liquids evaporated at a low temperature to dryness. The residue thus obtained is dissolved in a very small quantity of water, and the solution treated with slight excess of powdered acid sodium carbonate. The solution is now violently agitated in a stout test-tube or a small flask, with four or five volumes of pure ETHER, the mixture allowed to repose, and then a small portion of the clear supernatant ether transferred to a watch-glass and allowed to evaporate spontaneously.

If the transferred ether contained a *liquid* alkaloid in not too minute quantity, it will now remain in the watch-glass as oily

streaks, which, upon the application of a very gentle heat, collect into a drop and emit the peculiar pungent odor of the alkaloid (nicotine or conine), more or less masked by that of any animal matter present. If, however, a *fixed* alkaloid be present, there will be traces of a solid residue, destitute of any odor other than that of animal matter.

The alkaloid is liquid and volatile.—If traces of a volatile alkaloid are thus discovered, the contents of the vessel from which the small portion of ether was taken are rendered distinctly alkaline, and the whole violently agitated; after repose, the clear ether is separated by means of a pipette, and the residue washed in a similar manner three or four times with fresh portions of ether. The mixed ethereal liquids are now agitated with a small quantity of water containing sufficient diluted sulphuric acid to render the whole distinctly acid; the ether is then decanted, and the aqueous solution washed two or three times with fresh portions of ether.

By this treatment the aqueous solution will retain, in the form of sulphate, any volatile alkaloid present; while the decanted ether will remove such foreign matters as are soluble in that liquid. As, however, the sulphate of conine is not altogether insoluble in ether, this fluid may contain a small quantity of that salt.

The aqueous solution is now mixed with an excess of potassium or sodium hydrate, and again agitated with three or four volumes of pure ether, which will dissolve the liberated alkaloid, and also any ammonia present. The ether is then carefully decanted, the residue washed with a fresh portion of ether, the mixed ethers exposed to spontaneous evaporation at a low temperature, and the last trace of ammonia, if present, removed by placing the dish containing the residue for a few moments in vacuo over strong sulphuric acid, when the alkaloid will be left in its pure state. The exact nature of the alkaloid is then determined by appropriate tests.

The alkaloid is solid and fixed.—If the evaporation of the small portion of ether, taken from the mixture neutralized by acid sodium carbonate, does not indicate the presence of a volatile alkaloid, the original mixture is treated with excess of a fixed alkali, and again violently agitated; when the liquids have separated, the clear ether is decanted, the residue thoroughly extracted with fresh portions of ether, and the united ethereal liquids allowed to evaporate spontaneously at a low temperature. The residue thus obtained is some-

times in the solid form, but more frequently is a colorless milky liquid, in which are suspended small solid particles. It has usually a distinct alkaline reaction, and an offensive animal odor, which, however, is not pungent.

The residue is now treated with a few drops of alcohol, and the liquid allowed to evaporate spontaneously. If this fails to furnish the alkaloid in its crystalline form, a few drops of water feebly acidulated with sulphuric acid are added and gently rotated over the residue. This will convert the alkaloid into a sulphate of the base, which will dissolve; while any fatty matters present will usually remain undissolved and adhere to the sides of the dish. The liquid is cautiously decanted or filtered, the residue washed with a few drops of acidulated water, and the mixed liquids evaporated to a small volume in vacuo, or under a receiver over strong sulphuric acid. The concentrated liquid is then rendered alkaline by a concentrated solution of potassium or sodium carbonate, and the mixture treated with absolute alcohol, which will dissolve the liberated alkaloid, while the alkali sulphate formed, together with any excess of alkali carbonate present, will remain undissolved. The alcoholic solution is carefully decanted or filtered, and exposed to spontaneous evaporation, when the alkaloid will be left in its pure state. Its true nature is now determined by the appropriate reagents.

On applying the principles now described, M. Stas succeeded in isolating, when previously mixed with foreign organic matters, a great number of the alkaloids. And he also thus extracted morphine from opium; strychnine and brucine from nux vomica; veratrine from extract of veratrum; emetine from extract of ipecacuanha; colchicine from tincture of colchicum; aconitine from an aqueous extract of aconite; hyoscyamine from an old extract of henbane; and atropine from an old tincture of belladonna. (*Bulletin de l'Académie de Médecine de Belgique*, vi. 304.)

In applying the above method, the operator should bear in mind that the different alkaloids differ greatly in regard to their solubility in *ether*, and, therefore, that the quantity of this fluid necessary for their complete extraction from aqueous or alkaline mixtures will vary, other things being equal, with the nature of the base. In all cases, the quantity of a given substance that ether or any similar liquid will separate from its aqueous or alkaline solution—the quan-

tities of the different liquids being equal—will be in the same ratio as the solubility of the substance in the former menstruum exceeds its solubility in the latter.

For the extraction of most of the vegetable bases considered in the present treatise the method of Stas is very applicable; but for others it is only partially successful, or entirely fails, especially when the alkaloid is present in very complex mixtures. Thus, solanine requires something over six thousand times its weight of ether for solution, and therefore the quantity of this liquid necessary for the extraction of even a small quantity of the alkaloid is so great that it at the same time dissolves so much foreign matter as to render the ethereal residue unfit for the application of special tests. The same difficulty is also experienced in the separation of morphine, which in its crystalline state requires nearly eight thousand times its weight of ether for solution, and is at the same time somewhat soluble in alkaline fluids. This difficulty is removed to a considerable extent, as first suggested by Poellnitz, by *quickly* agitating the aqueous alkaline solution with ether and decanting this fluid before the morphine assumes the crystalline form. Again, in the case of nicotine, large quantities and repeated agitations with ether are required for its complete separation from aqueous solutions; since, although the alkaloid is very soluble in ether, yet it is also freely soluble in water. In the special consideration of the different alkaloids, their exact solubility in water and ether, as well as in chloroform, will be pointed out.

In the application of the above method for the detection of the fixed alkaloids, Prof. Otto strongly advises (*Detection of Poisons*, 160) to pursue much the same course as that advised for the recovery of the volatile or liquid bases. Thus, the organic mixture is treated with strong alcohol and oxalic or tartaric acid, and the whole gently heated; the cooled liquid is then filtered, the filtrate concentrated, the liquid again filtered, then evaporated to dryness, the residue extracted with absolute alcohol, the filtered extract evaporated to dryness, and the dry residue dissolved in a small quantity of water. All these operations are conducted in the same manner as before described.

Instead of now treating the aqueous solution—which contains the alkaloid in the form of a salt—with acid sodium carbonate or the caustic alkali, it is agitated with pure ether, and the operation

repeated as long as this liquid extracts any coloring matter; it is then treated with excess of a mineral alkali, and again agitated with ether, which will now dissolve the liberated alkaloid, and leave it, upon spontaneous evaporation, in its nearly or altogether pure state, and not unfrequently in the crystalline form.

Repeated experiments in our own hands with several of the fixed alkaloids have fully confirmed the advantages claimed by Prof. Otto for this process. Even granting that the ether takes up a trace of the alkaloidal salt, still, he remarks, this method deserves the preference, since a small quantity of the alkaloid in a pure state is infinitely more valuable for our purpose than a larger quantity in a state of impurity.

2. Method of Rodgers and Girdwood.

This process was recommended by its authors (*Lancet*, June, 1856, 718) simply for the recovery of strychnine, but, with slight modifications, it is equally applicable for the detection of most of the alkaloids. In principle it is much the same as the method of Stas, only that Chloroform instead of ether is used as the solvent of the liberated alkaloid. The details of this method are as follows:

The organic mixture, as the contents of the stomach, is treated with water acidulated with hydrochloric acid, and digested at a moderate heat for about two hours; when the mass has cooled, the liquid is separated by means of a muslin strainer, then filtered, and evaporated to dryness over a water-bath. The residue thus obtained is digested with strong alcohol containing a few drops of hydrochloric acid, the solution filtered, evaporated to dryness, and the residue extracted with distilled water. This aqueous solution is filtered, the filtrate supersaturated with ammonia, and the mixture agitated with about its own volume of *chloroform*. When the chloroform has completely subsided, it is transferred, by means of a pipette, to a small evaporating-dish, and evaporated to dryness. This residue contains any strychnine present, together with more or less foreign organic matter. To destroy the latter, the residue is moistened with concentrated sulphuric acid and allowed to remain over a water-bath for at least half an hour; the mixture is then treated with pure water, the filtered liquid rendered slightly alkaline with ammonia, and the alkaloid again extracted with chloroform.

The chloroform solution thus obtained usually contains the strych-

nine in a sufficiently pure state for special testing. If, however, a small portion of the liquid upon evaporation leaves a residue, which when moistened with concentrated sulphuric acid becomes charred, the whole of the chloroform is evaporated to dryness, and the residue again charred with sulphuric acid, in the manner just described, the alkaloid being again extracted from the alkaline liquid by chloroform.

A small portion of the separated chloroform is now allowed to evaporate drop by drop within as small a space as possible, in a white porcelain capsule. The residue thus obtained is tested in the ordinary manner.

In case the liver, spleen, or kidneys are the subject of analysis, the solid organ should be reduced to a pulp in a mortar previous to digestion in acidulated water. In the case of the tissues, if recent, they should be cut into very small pieces, and triturated in a similar manner.

As most of the alkaloids are much more freely soluble in chloroform than in ether, the former of these liquids is much better adapted than the latter for the separation of these poisons from organic mixtures.

3. Method of Uslar and Erdmann.

This process is founded on the fact that the free alkaloids are quite freely soluble in pure Amyl Alcohol; while, on the other hand, their hydrochlorides are insoluble in this menstruum, and therefore the former are readily removed from their solution in this liquid by shaking the mixture with water acidulated with hydrochloric acid. The manipulations according to this method are as follows:

The suspected mixture, made if necessary into a thin paste with water, is slightly acidulated with hydrochloric acid, and digested for one or two hours at a temperature of about 70° C. (158° F.). It is then transferred to a linen cloth which has been previously moistened with water, and when the liquid has passed, the residue is exhausted with hot water acidulated with hydrochloric acid, and the combined liquids treated with slight excess of ammonia, after which they are concentrated, first over a direct flame, then evaporated to dryness on a water-bath. The residue thus obtained is extracted three or four times with hot amyl alcohol, and the united solutions filtered through paper, previously moistened with the alcohol. The filtrate

has usually a yellow color, and contains, besides the alkaloid, fatty and coloring matters. To free it from the latter, the liquid is transferred to a cylindrical vessel, and violently agitated with several times its volume of nearly boiling water, acidulated with hydrochloric acid. By this operation the alkaloid is removed from its alcoholic solution, being taken up by the acidulated water, while the fat and coloring matter remain in the alcoholic liquid.

This fluid is now removed by means of a caoutchouc pipette, and the hot acid solution repeatedly extracted with fresh portions of the alcohol, until the fatty and coloring matters are completely removed; after which the clear aqueous liquid is concentrated somewhat by evaporation, then supersaturated with ammonia, and the mixture well shaken with fresh, hot amyl alcohol.

When the liquids have separated, the amyl alcohol, which now contains the free alkaloid, is removed by means of a pipette, and the acid solution again extracted with a fresh portion of the hot alcohol. The mixed alcoholic liquids are then evaporated to dryness on a water-bath, when the alkaloid will be left often in a sufficiently pure state for special examination. Should it, however, still present a yellowish or brownish color, it is again dissolved in very dilute hydrochloric acid, the solution agitated with a fresh portion of the hot alcohol, the latter liquid removed, and the aqueous solution treated with excess of ammonia, then shaken with hot amyl alcohol, and this fluid separated and evaporated as before.

The authors of this method cite a number of experiments in which, by it, they succeeded in recovering small quantities of morphine, narcotine, nicotine, conine, and strychnine, previously added to quite complex organic mixtures. In one of these experiments, about the third of a grain of morphine hydrochloride was added to a calf's stomach, and the latter exposed for a fortnight to the action of the sun and air; yet at the end of that time, although the mass had become thoroughly putrid, the alkaloid was recovered, and its presence indicated by the reaction of ferric chloride.

As morphine is quite soluble in *amyl alcohol*, while it is almost insoluble both in *ether* and in *chloroform*, the former of these liquids is very much better adapted than either of the latter for the separation of this alkaloid from organic mixtures. But for the separation of alkaloids about equally soluble in these three liquids we much prefer

the use of ether or chloroform to that of amyl alcohol, as the latter separates more slowly than either of the others from aqueous mixtures, and also requires a longer time for its evaporation. Moreover, as amyl alcohol requires a direct heat for its vaporization, any alkaloid present is much less likely to be left in its crystalline state than when it is deposited from ether or chloroform by spontaneous evaporation. Most of the alkaloids are more freely soluble in chloroform than in amyl alcohol.

4. Process of Graham and Hofmann.

This method was first advised by Profs. Graham and Hofmann for the detection of strychnine, when present, in beer; but it has since been extended by other experimenters to the separation of this and other alkaloids from other organic liquids. It takes advantage of the fact that when a solution of strychnine is agitated with Charcoal the latter absorbs the poison, and yields it up to alcohol when boiled with this liquid. The following are the details of the process, as first employed by its authors.

Two ounces of ivory-black, or animal charcoal, were shaken in half a gallon of beer to which half a grain of strychnine had been purposely added. After standing for about twelve hours, the liquid was found to be nearly deprived of all bitterness, the strychnine being absorbed by the charcoal. The liquid was now passed through a paper filter, upon which the charcoal containing the strychnine was collected and drained. The charcoal was then boiled for half an hour in eight ounces of ordinary spirits of wine, avoiding loss of alcohol by evaporation.

The alcoholic liquid thus obtained, which now contained the strychnine, was next filtered and afterward submitted to distillation. A residual watery fluid was thus obtained, holding the strychnine in solution, but not sufficiently pure for the application of tests. This solution was rendered alkaline by a few drops of a solution of potassium hydrate, and then agitated with an ounce of pure ether. The ethereal liquid, when separated and allowed to evaporate spontaneously in a watch-glass, left the alkaloid in a state sufficiently pure for testing. (*Quart. Jour. Chem. Soc.*, 1853, 173.)

Upon repeating this method, we find that from complex organic mixtures containing a very notable quantity of strychnine the alka-

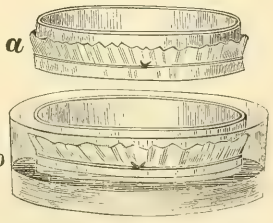
loid is extracted by the charcoal in a very nearly pure condition, or at most requires only one agitation with ether or chloroform to complete its purification; but when only a very minute quantity of the poison is present, it either entirely escapes detection or is so contaminated with foreign matter as to require as many extractions with ether or chloroform, for its purification, as to separate it by either of these liquids directly from the prepared original mixture. In all cases, according to our experience, this method is attended with greater loss of material than to prepare the mixture according to the process of Stas and then extract by chloroform.

5. Method by Dialysis.

Prof. T. Graham has shown that moist organic membranes possess the remarkable property of separating, when in solution, crystallizable substances from such as are uncrystallizable, the former readily passing through such membranes when surrounded by a liquid, whereas the latter entirely fail thus to pass, or do so only very slowly. (*Jour. Chem. Soc.*, 1862, 216.) The first of these classes, comprehending the crystallizable substances, he named *crystalloids*, the second *colloids;* and to this method of separation he applied the term *dialysis*. The most suitable substance for the dialytic septum is the material known as *parchment-paper*, which is prepared by immersing unsized paper for a few moments in a cold mixture of two measures of sulphuric acid and one of water.

For the application of this method, a light hoop of wood, or, better, of sheet gutta-percha, about two inches in depth and from five to ten inches in diameter, is covered with a piece of moistened parchment-paper, so as to form a sieve-like vessel (Fig. 12, *a*). The disk of paper used should exceed in diameter the hoop to be covered by three or four inches, so as to rise well up the outside of the hoop, and it should be bound to the hoop by a string or by an elastic band, but it should not be firmly secured. The parchment-paper must be entirely free from rents or pores. Its soundness may be ascertained by sponging the upper surface with pure water and then observing whether wet spots appear on

Fig. 12.



Graham's apparatus for the application of dialysis.

the opposite side: in case they do, the defects may be remedied by applying liquid albumen, and then coagulating this by heat. The vessel thus prepared is called the *dialyser*.

The liquid mixture to be examined is now poured into the dialyser, upon the surface of the parchment-paper, but only in such quantity as at most not to exceed about half an inch in depth. The vessel, with its contents, is then floated in a basin (*b*, Fig. 12) containing a quantity of pure water about four or five times greater than the volume of liquid in the dialyser. Any crystalloidal matter present, whether mineral or organic, will now begin to pass through the parchment-paper into the water in the larger vessel, and in twenty-four hours about two-thirds or more of it may be found in the outer liquid, or *diffusate*, as the latter is called. In most instances the diffusion is much promoted by the application of a gentle heat.

The diffusate is then concentrated, on a water-bath, to a small volume or evaporated to dryness, and the residue, if sufficiently pure, examined by appropriate reagents. If, however, the residue is unfit for special testing, as will usually be the case, at least in the case of the alkaloids, it is further purified by extraction with ether or chloroform, and then examined.

In a number of experiments by this method, for the separation of *small* quantities of different alkaloids from complex organic liquids, we were much disappointed in the results, they always falling far short of what we anticipated, especially in regard to the purity of the diffused alkaloid.

Even when the diffusate contains a quite notable quantity of the poison, the amount of colloidal or amorphous matter also present in the liquid is not unfrequently such as to require for its removal as many operations and as much labor as to extract the alkaloid at once from the original mixture by chloroform or ether, according to the methods previously considered. Moreover, when only a minute quantity of the vegetable base is present in the mixture submitted to examination, as a portion of the poison always remains in the dialyser, it may entirely escape detection, even when the quantity present in the original mixture is sufficient to give satisfactory results by the chloroform or ether method.

These results closely accord with those obtained in similar exper-

iments by Dr. Harvey and others. Some quantitative experiments in regard to the merits of this method for the extraction of small quantities of strychnine will be mentioned hereafter, in the special consideration of that alkaloid.

From the fact that in poisoning by metallic compounds the quantity present is generally much greater than in poisoning by vegetable substances, and, also, as the former usually diffuse somewhat more readily than the latter through membranes, dialysis seems better adapted, in medico-legal examinations, for the detection of mineral than of organic poisons.

6. Dragendorff's Method.

For the recovery of the alkaloids and allied principles from organic mixtures, Prof. Dragendorff has advised (*Gericht. Chem. Ermittel. Giften*, 1876, 141) to extract the finely divided substance with water acidulated with sulphuric acid at 40°–50° C. (104°–122° F.) for a few hours; this operation is repeated two or three times, and the strained and filtered liquids united. The mixed liquids are concentrated to a syrupy consistence, and the syrup mixed with three or four times its volume of alcohol and digested for twenty-four hours at about 30° C. (86° F.). The cooled liquid is filtered and the solids washed with 70 per cent. alcohol. The alcoholic liquid is distilled in a flask until the alcohol has been expelled, after which the cooled aqueous residue, diluted if necessary, is filtered.

For the examination of the extract thus prepared Prof. Dragendorff advises a very comprehensive method, by which not only the alkaloids but also various other vegetable principles would be recovered, the steps of the process being as follows:

I. The filtered liquid, while still acid, is violently agitated in a flask at the ordinary temperature with freshly rectified Petroleum Ether, which after the liquids have separated is decanted, and the operation repeated as long as the ethereal liquid takes up any matter. In this manner much of the *coloring matter*, and also, if present, *Piperine*, *Picric acid*, *Camphor*, and analogous bodies, constituents of *Black hellebore* and of *Aconite*, *Carbolic acid*, and certain essential oils, will be removed. Portions of the petroleum fluid may now be examined for these various substances.

II. The acid liquid is next agitated with Benzene, which in its turn is removed, and the operation repeated with a fresh volume

of benzene as long as a portion of the decanted liquid leaves a residue upon evaporation.

The *benzene* residue may contain any of the following substances: *Caffeine, Cantharidin, Santonin, Carophyllin, Cubebin, Piperine, Picric Acid, Aloetin, Digitalin, Cascarillin,* or *Berberine,* any of which may be left more or less crystalline. And also, as amorphous, *Elaterin, Populin, Colocynthin,* constituents of the *Pimento, Colchicine, Crysammic Acid,* or constituents of *Wormwood* and of certain other substances.

III. The acid aqueous solution is now extracted by CHLOROFORM in a similar manner. This liquid will extract, if present, *Cinchonine, Theobromine, Papaverine, Narceine, Picrotoxin, Helleborin, Digitalin, Convallamarin, Saponin, Senegin, Smilacin, Syringin,* or *Jervine* and other constituents of the *Hellebores.*

IV. The aqueous liquid is again agitated with PETROLEUM ETHER, for the purpose of removing the last traces of *Benzene* and *Chloroform.* After removal of the petroleum ether, the acid aqueous liquid is rendered *alkaline* by *Aqua Ammoniæ.*

V. The *ammoniacal liquid* is extracted with PETROLEUM ETHER, and the fluid decanted. The Petroleum residue may contain either *Strychnine, Quinine, Sabadilline, Brucine, Veratrine, Emetin, Conine, Methyl Conine, Nicotine, Alkaloid of Capsicum, Sarracinin, Lobeline, Sparteine, Trimethylamine, Aniline,* or the volatile alkaloid of *Pimento.*

VI. The aqueous ammoniacal liquid is now treated in like manner with BENZENE. This liquid will extract, if present, *Atropine, Hyoscyamine, Strychnine, Ethyl- and Methyl-Strychnine, Quinine and Quinidine, Cinchonine, Narcotine, Codeine, Acolyctin, Sabadilline, Thebaine, Brucine, Physostigmine, Veratrine, Sebatrin, Delphinine, Nepalin, Aconitine, Napellin, Emetin,* and the alkaloid of *Aconitum Lycoctonum.*

VII. The ammoniacal solution is next agitated with CHLOROFORM, which may extract *Morphine, Cinchonine, Papaverine, Narceine,* and the alkaloid of *Celandine.*

VIII. The alkaline liquid is now agitated with AMYL ALCOHOL, which will take up any *Morphine, Solanine,* or *Salicin* present; and, also, any *Narceine, Saponin, Senegin,* and *Convallamarin* that may not have been withdrawn in the previous extractions.

IX. Finally, the ammoniacal fluid is mixed with powdered

glass and evaporated to dryness, and the pulverized residue extracted by CHLOROFORM, which will dissolve any *Curarine* present.

Although the foregoing method of Dragendorff provides for the recovery of a great number and variety of organic substances, yet as very few, if any, of these bodies are *wholly insoluble* in the different extracting liquids employed, the substance, unless present in very notable quantity, might be entirely removed from the aqueous solution before the conditions best adapted for its recovery were reached.

For example, *morphine* and its sulphate are not absolutely insoluble in any of the liquids named, yet before employing the liquid in which this alkaloid is rather freely soluble, namely, amyl alcohol, the solution would have been extracted some *seven* different times with various liquids, and these employed to about exhaustion.

In regard to morphine, there is no doubt that if sufficient of the alkaloid is present to carry it through these various washings, that portion finally recovered by the amyl alcohol would be somewhat or even very much purer than if extracted at once from the prepared aqueous solution by rendering the latter alkaline and agitating it with the alcohol. But as to this quantity being present, especially of the absorbed poison, even under apparently the most favorable conditions, there is no certainty. Hence in medico-legal investigations we would hesitate to employ this method, at least in all its details; unless, perchance, there was no clue whatever, either from symptoms or other circumstances, as to at least the general nature of the poison taken. It very rarely happens that some knowledge of this kind is not at hand.

Recently Profs. Guareschi and Mosso (*Arch. Ital. Biol.*, 1883) have strongly objected to the method of Dragendorff, on the ground that on evaporation of the organic mixture the free sulphuric acid present may give rise to alkaloidal substances (ptomaines), due to the decomposing action of the acid. And this objection has been sustained by F. Coppola (*Gazzetta Chim. Ital.*, xii. 11, 511) in experiments on fresh dog's blood, examined after this method.

PTOMAINES.—This name was applied by Prof. Selmi to certain basic bodies or principles developed during the putrefactive decomposition of animal substances. Like principles have since been found in certain pathological conditions, and even, according to some ob-

servers, in normal tissues and secretions. The exact conditions under which these substances develop have not as yet been fully determined. The toxic symptoms produced by spoiled food may in some instances, perhaps, be due to the presence of these bodies.

Some of the ptomaines are said to be inert; others are more or less poisonous, producing in some instances symptoms similar to those occasioned by certain vegetable alkaloids. Some are described as liquid and volatile, others as fixed and crystallizable. For the most part they are more or less freely soluble in ether, in chloroform, and in benzene; but some are insoluble in one or more of these liquids. The ptomaine salts are generally freely soluble in water.

The ptomaines have usually an alkaline reaction, and yield precipitates with phosphomolybdic acid, iodized potassium iodide, platinic and auric chlorides, and with certain other general reagents for the alkaloids. In no instance has a substance of this kind been found that fully responds to the special reactions of any known vegetable alkaloid.

A very elaborate and important contribution to this subject has recently been made by Profs. Guareschi and Mosso (*Arch. Ital. Biol.*, 1883). In some preliminary experiments these observers found that commercial alcohol on evaporation with an acid very frequently leaves a residue having alkaloidal reactions; that a similar residue may be obtained from ordinary chloroform and ether; and that the purest commercial amyl alcohol and benzene contain pyridine. Hence these authors conclude that the results obtained by previous observers, in which these liquids, especially amyl alcohol and benzene, were employed for the extractions, have no value whatever.

From thirty-six kilogrammes (ninety-six pounds troy) of human brains, which had been allowed to putrefy at the ordinary temperature for about two months, Guareschi and Mosso obtained only a very minute quantity of ptomaines, the amount being too small, especially in view of the physiological experiments they desired to make, to determine its composition. Administered hypodermically to frogs in doses ranging from 0.0125 to 0.3 gramme (1–5th to 5 grains), this extract produced symptoms similar to those occasioned by curare; but it was much less energetic in its action, the latter quantity being required to prove fatal. According to these observers, the extract obtained from human brains could not be confounded in its properties with any known poison.

From eighty kilogrammes (two hundred and thirteen pounds) of fibrin from putrid ox-blood five months old an extract was obtained which had alkaloidal reactions, and a physiological action similar to the extract from human brains. On extracting fresh beef according to the method of Dragendorff, Profs. Guareschi and Mosso obtained a final residue which readily gave evidence of the presence of alkaloidal substances; whilst when tartaric acid was employed as the acidifying agent instead of sulphuric acid, a much smaller extract was obtained, and this had the properties of the extract from putrid fibrin. These results led these observers, as already stated, to condemn strongly the method of Dragendorff for medico-legal investigations.

Still more recently, F. Marino-Zuco (*Gazzetta Chim. Ital.*, xiii. 431) obtained from white and yolk of egg, brains, lungs, heart, liver, spleen, and blood, most carefully examined after several methods, all the conditions of the respective authors being observed, a basic substance having alkaloidal reactions and identical in composition with *neurine*. This neurine was found to originate, not, as is generally supposed, from alterations of the proteids, but from the splitting up of the lecithins under the influence of acids or alkalies. On applying the same method to the albumen remaining after complete extraction of the lecithins from egg, brain, lungs, and like substances, the result was purely negative.

Since neurine hydrochloride is not decomposed by acid sodium carbonate (bicarbonate), this author was able to separate completely the hydrochlorides of a vegetable alkaloid and of the so-called ptomaines by rendering the aqueous solution of the mixed salts alkaline by the sodium salt, and agitating the mixture with the proper solvent for the alkaloid. The alkaloid alone is thus extracted, the neurine remaining in the aqueous fluid as hydrochloride. (*Jour. Chem. Soc. Abst.*, March, 1884, 342.)

From the foregoing statements it is obvious that much uncertainty still exists in regard to the nature and production of the so-called ptomaines; yet, admitting their existence, there seems to be little danger of the experienced observer confounding these substances with the vegetable alkaloids, especially when the ordinary methods and pure reagents are employed for the extraction.

CHAPTER I.

VOLATILE ALKALOIDS: NICOTINE, CONINE

Section I.—Nicotine. (Tobacco.)

History.—Nicotine, nicotina, or *nicotia,* is the active principle of the common tobacco plant, *Nicotiana Tabacum,* in which it occurs in combination with malic acid; it exists in the leaves, root, and seeds of the plant, and also in the smoke of tobacco. Nicotine is destitute of oxygen, its formula being $C_{10}H_{14}N_2$. Vauquelin, in 1809, was the first to attempt the separation of this active principle, and he succeeded in discovering some of the properties of some of its compounds, but failed to isolate the pure alkaloid. Posselt and Reimann, in 1828, were the first to separate the alkaloid; in 1842, Ortigosa analyzed some of its compounds, and Barral analyzed nicotine itself. (*Gmelin's Hand-book,* xiv. 220.)

Preparation.—Nicotine may be prepared, as first proposed by M. Schloesing, in the following manner. Coarsely powdered tobacco is boiled with water, the cooled liquid strained through linen, then evaporated to the consistency of a syrup, and while hot agitated with twice its volume of alcohol of sp. gr. 0.837. After standing some time, the liquid portion of the mixture, which contains the whole of the vegetable base, is decanted from the black and almost solid deposit, then concentrated, and mixed, while still warm, with a solution of potassium hydrate, by which the alkaloid will be set free. The cooled mixture is agitated with ether, which will dissolve the liberated base, together with some coloring matter. After repose, the ethereal liquid is decanted and agitated with powdered oxalic acid, when, after a time, the oxalate of nicotine thus formed will subside as a syrupy mass. This, after the decantation of the ether, is washed with fresh ether, then rendered alkaline with potassium hydrate, and

again agitated with ether, which will now dissolve the alkaloid. The ethereal solution is transferred to a retort, the ether distilled off, and the residue exposed for some hours, at a temperature of about 140° C. (284° F.), to a current of hydrogen gas, by which the last traces of ether, water, and ammonia will be separated; the heat is then increased to about 180° C. (356° F.), when the alkaloid will distil over pure and colorless.

According to Dr. J. Skalweit, the process of Schloesing yields unreliable results for the quantitative determination of the nicotine present in tobacco, and he advises to convert the alkaloid into sulphate, and then extract this salt with 98 per cent. alcohol. (*Amer. Jour. Pharm.*, Feb. 1882, 60.)

The proportion of nicotine varies greatly in different kinds of tobacco. According to Schloesing (*Chem. Gaz.*, v. 43), some dried French samples contain from 7 to 8 per cent. of the alkaloid; Virginia and Kentucky, 6 or 7 per cent.; while Maryland and Havana contain only about 2 per cent., which is about the proportion found in ordinary snuff.

According to some observers, the *smoke* of tobacco does not contain nicotine; but Melsens has fully established the existence of the alkaloid in tobacco-smoke, and he places the quantity at about 0.7 per cent. of the weight of the tobacco consumed, and about 15 per cent. of the total quantity of nicotine contained in tobacco. (*Jour. Chem. Soc. Abst.*, Aug. 1882, 906.)

Nicotine is a transparent, colorless, oily liquid, and one of the most active poisons known, even equalling in the rapidity of its action hydrocyanic acid. There are, however, perhaps, only two instances yet recorded of poisoning of the human subject by this substance in its pure form; but poisoning by tobacco, which owes its activity entirely to this alkaloid, is not of unfrequent occurrence. The following consideration in regard to the physiological effects of the alkaloid will, therefore, be based chiefly upon its action as observed in cases of poisoning by tobacco.

Symptoms.—The usual effects produced by a poisonous dose of tobacco, when taken into the stomach, are confusion in the head, paleness of the countenance, vertigo, nausea, severe retching and vomiting, heat in the stomach, great anxiety, a sense of sinking at the pit of the stomach, with extreme prostration, trembling of the limbs, and sometimes violent purging. The pulse is small, feeble, and

almost imperceptible; the respiration difficult, and the skin cold and clammy; the pupils are generally dilated, but sometimes contracted, and the vision is usually more or less impaired. Death is often preceded by convulsions and paralysis.

In regard to the operation of tobacco, Dr. Pereira remarks that it resembles that of Lobelia inflata. With foxglove, tobacco agrees in several particulars, especially in that of enfeebling the action of the vascular system, though its power in this respect is inferior to that of foxglove. In its capability of causing relaxation and depression of the muscular system and trembling, tobacco surpasses foxglove; as it does, also, in its power of promoting the secretions. From belladonna, stramonium, and hyoscyamus it is distinguished by causing contraction of the pupil, both when applied to the eye and when taken internally in poisonous doses, and also by the absence of delirium and of any affection of the parts about the throat. (*Mat. Med.*, ii. 494.)

A singular case is related (*Jour. de Chim. Méd.*, 1869, 565) in which a man accustomed to smoking took into his mouth for the first time a bolus of tobacco, and after a quarter of an hour involuntarily swallowed the mass. An hour later he became unconscious, and, although the usual remedies were employed, he became worse and expired, without at any time having recovered consciousness.

Administered in the form of *clyster*, tobacco has in several instances caused death. In a case of this kind quoted by Dr. Christison, in which an enema prepared by boiling about an ounce of tobacco for fifteen minutes in water was administered by the advice of a quack to an individual laboring under obstinate constipation, the patient was seized in *two minutes* afterward with vomiting, violent convulsions, and stertorous breathing, and died in three-quarters of an hour.

So, also, the *external* application of tobacco to abraded surfaces, and even to the healthy skin, has been attended with violent symptoms, and even death. In a case of this kind, in which a man applied to himself a decoction of tobacco for the cure of an eruptive disease, death took place in three hours with the usual symptoms of tobacco poisoning. (See *Amer. Jour. Med. Sci.*, Jan. 1865, 268.)

Even the *smoking* of tobacco has been known to produce dangerous and even fatal results. Dr. Marshall Hall relates the case of a young man, who, having smoked two pipes of tobacco, was seized

with nausea, vomiting, syncope, stupor, stertorous breathing, and general spasms: after a time he recovered. Gmelin mentions two cases of death, caused in one instance by the smoking of seventeen, and in the other of eighteen, pipes of tobacco at a sitting. In another case, in which a man during a period of less than twelve hours smoked forty cigarettes and fourteen full-sized cigars, death took place from the effects on the evening of the following day.

A most remarkable case of poisoning by *nicotine* in its pure state occurred in Belgium, in 1850, for which the Count de Bocarmé was condemned to death, the person murdered being his brother-in-law, Gustave Fougnies. An unknown quantity of the poison was forcibly administered, and it is believed that death took place within five minutes afterward. Nicotine was detected in small quantity by M. Stas in the mouth, throat, stomach, liver, and spleen of the deceased, and also in the floor near which the act was committed. (*Orfila's Toxicology*, ii. 498.) The only other related case of poisoning by this alkaloid in its pure state occurred in London, in 1858, and death took place in from three to five minutes after the poison had been taken. In this case a small quantity of the poison was detected by Dr. Taylor in the contents of the stomach.

Experiments.—In this connection, we may briefly relate the following experiments in regard to the action of *nicotine* in its pure state upon animals. (*a*) One drop of the poison placed in the mouth of a full-grown cat produced *immediate* prostration, continued convulsive movements of the extremities, and death in *seventy-eight seconds* after the poison had been administered. (*b*) In another case, a small drop was placed on the tongue of a cat. In *ten seconds* the animal fell on the right side perfectly prostrated, then had convulsive movements of the legs, voided urine, and died in two minutes and a half. (*c*) A third cat, to which a similar quantity had been administered, fell in about *twelve seconds*, had violent convulsions of the extremities, and was dead in *seventy-five seconds* after taking the poison.

Period when Fatal.—In fatal poisoning by *tobacco*, death does not usually occur until after some hours, but it may take place within a very much shorter period. In a case in which about an ounce of crude tobacco had been swallowed, death took place in about seven hours; while in another, an unknown quantity of snuff administered in whiskey proved fatal in about one hour.

Most of the reported cases of death from tobacco have been occasioned by its use in the form of clyster. M. Tavignot relates a case in which an injection prepared by mistake with nearly two ounces of tobacco (sixty grammes), instead of nine grains and a quarter (sixty centigrammes), was administered to a stout man, aged fifty-five years. In seven or eight minutes afterward he was seized with stupor, headache, paleness of the face, pain in the abdomen, indistinct articulation, and convulsive tremors, at first of the arms, then of the whole body. These symptoms were soon followed by extreme prostration and slow laborious breathing, and then coma, which terminated fatally in about *eighteen minutes* after the injection had been administered. (*Gazette Méd. de Paris*, Nov. 1840, 763.) In a case quoted by Dr. Beck (*Med. Jur.*, ii. 878), a female affected with worms used an enema of tobacco, and was soon seized with violent convulsions, and died from its effects *fifteen minutes* afterward.

Fatal Quantity.—In most of the fatal cases of poisoning from the swallowing of tobacco, the quantity taken could not be accurately determined. In a case reported by Mr. Skae, a man who had swallowed a large mouthful of crude tobacco became suddenly insensible, motionless, and relaxed, with contracted pupils, and a scarcely perceptible pulse. These symptoms were followed by convulsions, loud cries, dilated pupils, active vomiting and purging, and death by syncope. (*Stillé's Mat. Med.*, ii. 298.)

Administered in the form of *enema*, tobacco has proved fatal in comparatively small quantity. Thus, several instances are reported in which a decoction of a drachm exhibited in this manner caused death. In one of these, quoted by Dr. Christison, death took place in thirty-five minutes. In a case cited by Dr. Pereira (*Mat. Med.*, ii. 494), an injection containing only half a drachm was followed by fatal results.

Treatment.—This consists in the speedy removal of the poison, in case it has been swallowed, from the stomach; and the subsequent exhibition of stimulants. Animal charcoal, tannic acid, and an aqueous solution of iodine in potassium iodide have been advised as chemical antidotes. Opium may sometimes be found useful to allay the excessive vomiting.

Post-mortem Appearances.—These are subject to great variation. In a case quoted by Dr. Taylor (*On Poisons*, 747), in which

something less than an ounce of crude tobacco had been swallowed and death occurred in about seven hours, the following appearances were observed forty hours after death. The substance of the brain and the upper part of the spinal marrow were somewhat congested; the heart was empty, small, and contracted; and the liver and kidneys were much congested. The mucous membrane of the stomach presented several red patches. The intestines were contracted throughout, and contained only a mucous fluid tinged with blood; the mucous membrane was of a red color, partially abraded, and full. The bladder was contracted and empty. The blood throughout the body was dark-colored and liquid.

In a case in which an enema prepared with about an ounce of tobacco proved fatal in three-quarters of an hour, the only abnormal appearances observed two days after death were a gorged condition and redness of the inner and outer coats of the large and small intestines, and patches of extravasation in some parts of the mucous membrane, together with an empty state of the heart and of the blood-vessels of the abdomen. The stomach and brain were natural.

Chemical Properties.

General Chemical Nature.—*Nicotine*, when perfectly pure, is a transparent, colorless, oily liquid, having a strong alkaline reaction, and a density of about 1.048. Its odor is usually described as acrid, unpleasant, and resembling somewhat that of tobacco: this is true of most samples as met with in the shops, but when perfectly pure it has, as remarked by Otto, a rather pleasant ethereal odor. The odor may be perceived, but is not characteristic, in a few drops of a pure 1–50,000th aqueous solution of the alkaloid.

Nicotine has a pungent, acrid taste, even when highly diluted, producing a peculiar sensation in the throat and air-passages. It slowly distils at about 146° C. (295° F.), and boils at about 243.5° C. (470° F.), recondensing for the most part unchanged; in an atmosphere of hydrogen gas it may be distilled without any decomposition. It imparts a transient greasy stain to white paper, and burns with a white, smoky flame. On exposure to the air, nicotine slowly becomes yellow, then brownish and thick, being finally converted into a resinous mass.

Solubility.—Nicotine is freely soluble in all proportions in water; it is also soluble in alcohol, ether, chloroform, the fixed oils, and in

oil of turpentine. By the use of some of these latter solvents the alkaloid may be extracted to a greater or less extent from its solution in water. For this purpose ether has usually been employed, but this liquid is inferior in this respect to chloroform, as may be seen from the following experiments.

1. *Extraction by Ether.*—When one volume of a 1–100th aqueous solution of nicotine is agitated with *five* volumes of *absolute ether*, and the latter liquid, after repose, decanted, the aqueous solution yields with reagents somewhat better reactions of the presence of nicotine than a pure 1–500th solution of the alkaloid; thus showing that the ether extracted less than four-fifths of the vegetable base. When a 1–100th solution is agitated with *twenty-five* volumes of ether, the aqueous liquid is reduced to about a 1–1200th solution. Experiments made with aqueous solutions of the hydrochloride of nicotine, by decomposing the salt with potassium hydrate and then extracting with absolute ether, gave results similar to those just mentioned; as did also experiments in which concentrated commercial ether was employed as the extracting liquid.

2. *By Chloroform.*—When a 1–100th aqueous solution of pure nicotine is agitated with *five* volumes of pure chloroform, and the latter carefully decanted, the former liquid is reduced to about a 1–4000th solution of the alkaloid. So, also, under like circumstances, a 1–1000th aqueous solution is reduced to about a 1–40,000th solution. These experiments show that under these conditions chloroform separates about 39-40ths of the alkaloid.

Special Chemical Properties.—If a drop of nicotine be placed in a watch-glass, and this covered by a similar, inverted glass containing a small drop of either hydrochloric or nitric acid, the glasses become filled with white fumes. These fumes are not so dense as those obtained from conine under similar circumstances; nor are they, as in the case of conine, attended with the formation of crystals. When the pure alkaloid is treated directly with concentrated hydrochloric acid, it yields a syrupy liquid, without the formation of crystals; with nitric acid it yields a reddish syrupy fluid. When the alkaloid is touched with concentrated sulphuric acid, it undergoes little or no change until the mixture is heated, when it acquires a brownish color. It need hardly be added that these reactions in themselves are not characteristic of this alkaloid.

A pure *aqueous* solution of nicotine is colorless, has the peculiar

odor and taste of the alkaloid, and an alkaline reaction. When such a solution is distilled, the alkaloid passes over with the vapor of water. Nicotine readily unites with acids, forming salts, some of which are readily crystallizable.

The *salts* of nicotine have the peculiar taste of the alkaloid, but are destitute of odor. They are mostly soluble in water and in alcohol, but insoluble in ether. Their aqueous solutions lose part of the alkaloid upon evaporation, and are decomposed by the mineral alkalies, evolving the odor of nicotine. When such an alkaline mixture is agitated with chloroform, this liquid, after decantation and evaporation, leaves the extracted alkaloid in the form of oily drops or streaks. On distilling a solution of a salt of nicotine which has been treated with excess of potassium or sodium hydrate, the free alkaloid will be found in the distillate, together with any ammonia that may have been present in the mixture. If the distillate thus obtained be neutralized with oxalic acid, then gently evaporated to dryness, and the residue treated with alcohol, this liquid will dissolve the oxalate of nicotine produced by the neutralization, while any ammonium oxalate present will remain, it being insoluble in this menstruum. On now evaporating the alcoholic solution to dryness, the oxalate of nicotine may be obtained in its pure state.

In the following examinations of the limit of different tests for nicotine when in solution, the pure, colorless alkaloid was dissolved in distilled water. The fractions indicate the fractional part of a grain of the alkaloid in solution in *one grain* of water. The results, except when otherwise stated, refer to the behavior of *one grain* of the solution.

1. *Platinic Chloride.*

This reagent throws down from somewhat strong aqueous solutions of nicotine and of its salts a yellow precipitate of the double chloride of platinum and nicotine, having, according to Ortigosa, the composition $C_{10}H_{14}N_2,2HCl$; $PtCl_4$. The precipitate produced from aqueous solutions of the free alkaloid by the pure reagent is at first amorphous, but after a little time it becomes, in part at least, crystalline. But when from solutions of the hydrochloride of nicotine, or if the reagent contains free hydrochloric acid, the precipitate immediately assumes the crystalline form. From more dilute solutions of the alkaloid or of its salts the precipitate separates only after a time, and then in the crystalline state; its separation is much facilitated

by stirring the mixture. The precipitate, in its crystalline form, dissolves but slowly in large excess of hydrochloric acid; in its amorphous condition, however, it is much more readily soluble. It is insoluble in acetic acid, in alcohol, and in ether, but soluble in excess of free nicotine. The crystals are permanent in the air.

1. $\frac{1}{100}$ grain of nicotine, in one grain of water, yields with the reagent a quite good deposit of orange-yellow crystals, Plate VI., fig. 1.
2. $\frac{1}{500}$ grain: after a little time the mixture becomes turbid, and ultimately yields small crystals of the double salt. If the mixture be stirred with a glass rod, it very soon yields granular streaks on the dish or glass-slide over the path of the rod, and in a little time a quite satisfactory crystalline deposit.

Platinic chloride also produces yellow crystalline precipitates in solutions of potassium hydrate and of ammonia; but the forms of the crystals thus produced are wholly different from those of the double nicotine salt. (Compare Plate I., fig. 1.) The application of some of the tests, such as the iodine reagent, which produce precipitates with nicotine but none with the inorganic alkalies, would also readily distinguish the former from the latter. If the solution under examination has been prepared by extraction from a suspected mixture by chloroform or ether, then a mineral alkali could not be present, since they are insoluble in these liquids.

This reagent also throws down yellow precipitates from solutions of most of the other alkaloids, some of which, like the nicotine deposit, are crystalline; but in no instance have the crystals the same microscopic forms as those obtained from somewhat strong solutions of nicotine. The production of this crystalline precipitate, together with the odor and physical state of nicotine, readily serves to distinguish this alkaloid from all other substances.

2. *Mercuric Chloride.*

Mercuric chloride, or *corrosive sublimate*, produces in strong solutions of nicotine a copious, white, curdy precipitate, which soon acquires a yellow color and deposits beautiful groups of colorless crystals, which are permanent in the air. The precipitate produced from somewhat dilute solutions of the alkaloid remains white, and after a time yields the same crystals as from strong solutions. These precipitates are readily soluble in hydrochloric and acetic acids. The

white precipitate is soluble in ammonium chloride, from which, after a time, it is redeposited; the yellow precipitate is immediately decolorized by ammonium chloride and, in part at least, dissolved, but after a time it separates in the form of a white powder. The precipitates are to a greater or less extent dissolved upon the application of heat, but again reproduced as the solution cools.

1. $\frac{1}{100}$ grain of nicotine, in one grain of water, yields a copious, white precipitate, which in a little time becomes yellow and yields a mass of large groups of crystals, Plate VI., fig. 2. These crystals are especially beautiful under polarized light.
2. $\frac{1}{500}$ grain yields a rather copious, dirty-white precipitate, which soon deposits colorless crystals.
3. $\frac{1}{1000}$ grain: in a few seconds the mixture becomes turbid, and soon there is a quite good, white, flocculent precipitate, which after a time yields crystals having the same forms as illustrated above. If upon the addition of the reagent the mixture be stirred with a glass rod, it immediately yields streaks on the bottom of the watch-glass over the path of the rod, and soon innumerable opaque granules and granular masses appear, which after a little time present the appearances illustrated in the lower portion of the above figure.
4. $\frac{1}{2500}$ grain: if the mixture be stirred and allowed to stand, it yields after some time quite a number of large crystalline groups.

Although corrosive sublimate also produces white precipitates with ammonia and various inorganic substances, as well as with most of the alkaloids and many other kinds of organic matter, yet all these deposits, unlike that from nicotine, remain amorphous, except the precipitate from strychnine, and in this case the crystals, which are usually obtained with difficulty, are always of a wholly different form from those produced by the nicotine deposit. (Compare Plate XI., fig. 2.) It may be added that the nicotine precipitate is very readily soluble in excess of acetic acid, whereas the strychnine compound is soluble with difficulty in this acid.

We have found, in repeated experiments, that the precipitate produced by this reagent from quite impure solutions of nicotine will after a time yield characteristic crystals, even in the midst of a dense deposit of foreign matter. Nevertheless, it must be borne in mind that under these circumstances the precipitate may fail to crystallize. In applying this test to somewhat complex organic

liquids, the precipitate should be stirred and allowed to stand for at least an hour, with the occasional addition of very small quantities of pure water to prevent the deposit becoming dry, before it is fully concluded that crystals will not form.

This is the most valuable test yet known for the detection of nicotine when in solution.

3. *Picric Acid.*

An alcoholic solution of *picric*, or *carbazotic, acid*, throws down from aqueous solutions of nicotine a yellow, amorphous precipitate, which soon becomes a mass of crystalline tufts. It is necessary to use large excess of the reagent, otherwise either no deposit will form, or if produced it will soon disappear.

1. $\frac{1}{100}$ grain of nicotine yields an immediate yellow or greenish-yellow precipitate, which soon becomes a mass of groups of yellow, crystalline tufts, Plate VI., fig. 3.
2. $\frac{1}{1000}$ grain: a rather copious precipitate, which soon crystallizes.
3. $\frac{1}{10,000}$ grain yields a very good crystalline precipitate.
4. $\frac{1}{40,000}$ grain yields a just perceptible precipitate.

This reagent also throws down from solutions of the inorganic alkalies, and of several of the other alkaloids, besides nicotine, yellow precipitates which become crystalline. But by the aid of the microscope the crystallized nicotine compound may generally be readily distinguished from all of these deposits except that produced from very strong solutions of sodium hydrate (Plate I., fig. 6), which has frequently much the same crystalline form as that assumed by the nicotine salt. Any doubt as to the true nature of the deposit may, of course, be readily removed by the application of other reagents.

This reagent will often produce crystals with only the 1–10,000th of a grain of nicotine, in one grain of water, in the presence of foreign organic matter. But in mixtures of this kind the formation of crystals is more readily interfered with than in the application of the preceding reagent.

4. *Iodine in Potassium Iodide.*

This reagent may be prepared by dissolving five parts of potassium iodide in one hundred parts of water, and then adding two

parts of pure iodine. A drop or two of this mixture throws down from solutions of nicotine and of its salts a reddish-brown, brownish-yellow, or yellowish, amorphous precipitate, its exact color depending somewhat upon the strength of the alkaloidal solution, and also upon the quantity of reagent added. After a little time the precipitate may entirely disappear; but it is immediately reproduced upon further addition of the reagent. The precipitate is readily soluble in potassium hydrate and in alcohol.

1. $\frac{1}{100}$ grain of nicotine, in one grain of water, yields a very copious deposit.
2. $\frac{1}{1000}$ grain: a copious, reddish-brown precipitate.
3. $\frac{1}{10,000}$ grain yields a good reddish-yellow deposit.
4. $\frac{1}{25,000}$ grain: a quite distinct greenish-yellow precipitate.
5. $\frac{1}{50,000}$ grain: a quite good turbidity.
6. $\frac{1}{100,000}$ grain: a very obvious turbidity.
7. $\frac{1}{250,000}$ grain yields a perceptible cloudiness.

As a solution of iodine in potassium iodide causes no precipitate in solutions of the inorganic alkalies and has its color immediately discharged by them, it readily serves to distinguish nicotine from these substances. But, as the reagent produces with most of the alkaloids and many other substances precipitates similar to that from nicotine, it has no positive value, for the detection of this alkaloid, further than to confirm the reactions of other tests.

From the fact that the limit of the reaction of this reagent exceeds that of either of the other tests for nicotine, it is obvious that should this test fail to produce a precipitate, in a solution suspected to contain nicotine, it would be fruitless to apply any of the other tests to the same solution, unless possibly there should be some substance present that interfered with the reaction of this reagent.

5. *Auric Chloride.*

Trichloride of gold produces in aqueous solutions of nicotine a yellow, amorphous precipitate, which is nearly insoluble in acetic and hydrochloric acids, but soluble, to a clear solution, in excess of the caustic alkalies.

1. $\frac{1}{100}$ grain of nicotine yields an immediate, copious, yellow precipitate, which remains amorphous; the deposit is not entirely soluble in several drops of strong acetic acid. If several grains or more of the nicotine solution be precipitated by the reagent

and the mixture then heated, the precipitate dissolves to a beautiful purple solution.

2. $\frac{1}{1000}$ grain yields a good, yellow deposit, which is slowly soluble in a few drops of a strong solution of potassium hydrate. If the precipitate produced from several grains of the solution be heated in the mixture, it dissolves, and is reproduced unchanged as the mixture cools.
3. $\frac{1}{5000}$ grain: an immediate greenish-yellow precipitate, which soon increases to a quite good, dirty-yellow deposit; the precipitate is readily soluble in a drop of potassium hydrate solution.
4. $\frac{1}{10,000}$ grain yields a good, yellowish precipitate, which immediately disappears upon the addition of an alkali.
5. $\frac{1}{25,000}$ grain: in a few moments a distinct turbidity, and in a little time a quite satisfactory precipitate.
6. $\frac{1}{50,000}$ grain: in a little time the mixture becomes turbid, and soon there is a quite distinct deposit.

Trichloride of gold also produces yellow, amorphous precipitates with most of the alkaloids and various other substances.

6. *Bromine in Bromohydric Acid.*

Aqueous solutions of nicotine yield with a strong aqueous solution of bromohydric acid saturated with bromine a yellow, amorphous precipitate, which in a little time disappears.

1. $\frac{1}{100}$ grain of nicotine yields a copious, bright yellow precipitate, which soon disappears, but is reproduced upon further addition of the reagent.
2. $\frac{1}{1000}$ grain: a rather copious precipitate.
3. $\frac{1}{5000}$ grain yields a very good, greenish-yellow deposit, which soon dissolves, and is not reproduced upon further addition of the reagent.
4. $\frac{1}{10,000}$ grain yields a slight turbidity.

The reaction of this reagent is common to most of the alkaloids and many other organic compounds. The reagent produces no precipitate and has its color discharged when added to solutions of the caustic alkalies.

7. *Tannic Acid.*

Tannic acid produces in aqueous solutions of nicotine a white, amorphous precipitate, which readily dissolves to a clear solution on

the addition of a small quantity of hydrochloric acid, but is reproduced upon further addition of the acid, and is then insoluble in large excess. The precipitate is readily soluble in acetic and nitric acids, without being reproduced upon further addition of the acid.

1. $\frac{1}{100}$ grain of nicotine, in one grain of water, yields a copious precipitate.
2. $\frac{1}{1000}$ grain: a good, bluish-white deposit.
3. $\frac{1}{10,000}$ grain: the mixture becomes slightly turbid.

This reagent also throws down white precipitates from solutions of very many other substances. The behavior of the nicotine precipitate with hydrochloric acid, however, is somewhat peculiar.

Other Reactions of Nicotine.—As nicotine has strong basic properties, it, like the caustic alkalies, precipitates the oxides of many of the metals from solutions of their salts. *Mercurous nitrate* throws down from somewhat strong solutions of the free alkaloid a copious, dirty-yellow precipitate, which almost immediately becomes brown, then nearly black: this transition of color is due to the successive reduction of the precipitated oxide of mercury. With one grain of a 1–5000th solution of the alkaloid this reagent produces a rather good, dirty-white precipitate.

Sulphate of copper produces with aqueous solutions of the alkaloid, when not too dilute, a bluish, flocculent precipitate of the oxide of copper, which is insoluble in excess of nicotine. The statement of some writers that this precipitate dissolves in excess of the pure alkaloid to a blue solution, similar to that formed by ammonia, is certainly erroneous. Solutions of salts of lead, silver, nickel, cobalt, and several other metals also produce precipitates from somewhat strong solutions of the alkaloid. A 1–100th solution of nicotine yields with silver nitrate a quite good, white precipitate, which but very slowly darkens upon exposure to sunlight.

Solutions of nicotine, even when concentrated, fail to yield a precipitate with either potassium sulphocyanide, the chromates of potassium, ferro- or ferri-cyanide of potassium, or gallic acid.

Separation from Organic Mixtures.

In suspected poisoning by tobacco, before proceeding to the chemical examination for nicotine, the analyst should carefully examine the suspected mixture or contents of the stomach for the

presence of tobacco in its solid state. Any portions of the plant thus found, separated from all adhering matter, should be carefully examined, by means of the microscope if necessary, in regard to their botanical characters, then digested at a gentle heat in acidulated water, and the solution examined in the manner just to be described.

Suspected Solutions and Contents of the Stomach.—The mixture submitted for examination, diluted with distilled water if necessary, is slightly acidulated with acetic acid and digested for some little time at a moderate heat; it is then allowed to cool, the liquid strained through muslin, the solids on the muslin washed with water and well pressed, and the united strained liquids filtered. The clear liquid is now evaporated to a small volume on a water-bath, then mixed with about an equal volume of strong alcohol, and the mixture gently warmed for some minutes with constant stirring; the cooled liquid is again filtered, and the filtrate evaporated on a water-bath to very near dryness. Any nicotine originally present will now be in the residue in the form of acetate of the alkaloid.

This residue is gently warmed with about a fluid-drachm or even less of pure water, the mixture thoroughly stirred, transferred to a wet paper filter, and the filtrate collected in a stout test-tube. The contents of the tube are now rendered alkaline by a few drops of potassium or sodium hydrate, when the nicotine will be liberated from its saline combination, and perhaps emit its peculiar odor.

The mixture is now violently shaken for some minutes with about two volumes of *chloroform* or about five volumes of *ether*, and this mixture allowed to repose until the fluids have completely separated. In case chloroform has been used as the solvent of the liberated alkaloid, the supernatant aqueous fluid is removed by means of a pipette, the chloroform carefully decanted into another perfectly dry test-tube, and from this into a large watch-glass. By these decantations, any globules of water which may have escaped removal by the pipette may, by care, be made to adhere to the sides of one or other of the test-tubes. Should, however, globules of the alkaline aqueous fluid have passed along with the chloroform into the watch-glass, these must be removed before the latter liquid is evaporated to dryness, otherwise the residue will contain a trace of the fixed alkali, which might subsequently interfere with some of the tests for nicotine. The alkaline aqueous liquid removed by the pipette is now washed with something less than its own volume of fresh chloroform, and this, after

repose, decanted and added to the first chloroform extract. If ether has been employed as the solvent of the alkaloid, the aqueous fluid is agitated a second time with two or three volumes of ether, and the united ethereal liquids carefully collected in a large watch-glass.

The contents of the watch-glass are now allowed to evaporate spontaneously, in a cool place, when any nicotine present will be left in the form of oily drops or streaks, having the peculiar odor of the alkaloid, especially upon the application of a very gentle heat. As the residue from extracts of this kind has frequently a strong animal odor, this may more or less conceal that of the poison.

If the residue thus obtained indicates the presence of a comparatively large quantity of the alkaloid, the contents of the watch-glass are stirred with about half a drachm or more of pure water, and the mixture, if it contains white, flocculent masses, or if turbid, transferred in small portions to a very small moistened filter: when the whole of the fluid has passed through, the filter is washed with a few drops of water and this collected with the first filtrate. If, on the other hand, the chloroform residue fails to reveal any distinct evidence of the presence of the alkaloid, only a few drops of water are used for its solution.

A drop of the clear liquid, transferred by means of a pipette to a watch-glass, may now be treated with a small drop of corrosive sublimate solution, the mixture allowed to stand quietly for some little time, and then examined by the microscope. If this examination indicates the presence of nicotine, other portions of the clear liquid may be examined by platinic chloride, picric acid, and any of the other tests for this alkaloid. If, however, the corrosive sublimate mixture fails to yield crystals, it should be stirred with a glass rod, and allowed to stand half an hour or longer. Should it still fail to yield any evidence of the presence of the poison, the original liquid may be concentrated, and then a drop examined by this reagent. On the other hand, should this test as first applied indicate the presence of much foreign matter, the original solution is again extracted by chloroform, this liquid evaporated to dryness, and the residue treated as before.

By the method now considered, nicotine was detected in very notable quantities in the stomachs of the first two cats before referred to (*ante*, 437), each of which was killed by a single drop of the alkaloid placed in the mouth of the animal. And by it we have also

obtained perfectly satisfactory evidence of the presence of the poison in an ounce of a very complex organic mixture, to which only the 1–100th of a grain of the alkaloid had been added.

From the Tissues.—For the separation of absorbed nicotine from the tissues, the solid organ, such as the liver, spleen, or lungs, is cut into very small shreds, then made into a thin paste with water, the mixture acidulated with acetic acid, and digested, with frequent stirring, for some time at a very gentle heat. The cooled mixture is then treated in the same manner as before described for the examination of suspected solutions.

As the quantity of the alkaloid present in the tissues, in poisoning by this substance, is at most extremely small, the residue obtained from the chloroform extract should be treated with only a few drops of water, and great care exercised in the preparation of this solution for the application of the different tests.

M. Stas was, perhaps, the first to show that nicotine was absorbed and might be separated from the tissues in its unchanged state. The same fact was also pointed out about the same time by Orfila. This observer cites several instances (*Toxicologie*, 1852, ii. 493) in which he obtained the poison from the liver and spleen of dogs killed by from fifteen to twenty drops of the alkaloid.

From the Blood.—Nicotine, when present in the blood, may be recovered by acidulating the liquid with about five drops of strong acetic acid for each ounce of fluid, and agitating it in a closed bottle with about its own volume or more of a mixture of equal parts of water and alcohol, until the whole becomes perfectly homogeneous. The mixture is then digested at a moderate heat, with frequent stirring, until the albuminous matter present collects into small brownish flakes. The cooled liquid is strained through wet muslin, and the solid residue washed and strongly pressed. If the liquid is still turbid, it is passed through the strainer a second or even a third time. The fluid is now evaporated at a moderate heat on a water-bath to about half its volume, and while still warm mixed with a little strong alcohol, and the reddish-brown, coagulated matter removed by a muslin filter. When the quantity of blood operated upon is comparatively small, the strained liquid thus obtained is usually clear and has only a slight yellow color; but when a large amount of the fluid is examined, the strained liquid is generally turbid and highly colored. Under these circumstances it may be passed through a wet paper filter.

The liquid is now slowly evaporated on a water-bath to near dryness. If during the concentration much solid matter separates, it should be removed by a small filter. The nearly dry residue is stirred with about half a drachm of water, the solution filtered, the filtrate rendered alkaline by sodium hydrate, and extracted by chloroform in the usual manner. The chloroform residue is well stirred with a few drops of water, and the liquid carefully separated from any flakes of animal matter present, either by means of a pipette or by a very small filter. The liquid is then examined by the ordinary reagents.

By the above method, perfectly satisfactory evidence of the presence of nicotine was obtained from one ounce of healthy blood to which the 1–100th of a grain of the alkaloid had been purposely added,—the dilution being one part of the poison in about 50,000 parts of the fluid.

In the case of the second of the three cats before referred to,—in which a small drop of nicotine proved fatal in two minutes and a half,—seven fluid-drachms of blood were recovered from the body immediately after death; five drachms of the liquid were then treated after the above method, and the final aqueous solution reduced to three drops. One drop of this mixture, when treated with corrosive sublimate, gave after a little time perfectly satisfactory evidence of the presence of nicotine, it yielding about twenty large groups of crystals similar to those shown in Plate VI., fig. 2. A second drop, treated with picric acid, also furnished a fine deposit of characteristic crystals. The third drop gave with platinic chloride a slight precipitate, but no crystals were obtained.

From the third cat—which was killed in *seventy-five seconds* by a drop of the alkaloid—ten fluid-drachms of blood were obtained with the greatest possible speed and care, and then treated as before described, except that a drop of sulphuric acid was used as the acidifying agent, and *ether* for the extraction of the poison. The final solution, when reduced to two drops, gave with corrosive sublimate and picric acid perfectly satisfactory evidence of the presence of the alkaloid, but at the same time indicated that it was present in smaller quantity than in the preceding case. This case shows the extreme rapidity with which this poison may enter the circulation.

It is a singular fact that the chloroform and ether residues in

both the foregoing cases possessed in a very marked degree the peculiar ethereal odor of the pure alkaloid administered; whilst in another case, in which the poisoning was occasioned by an extract of tobacco, the chloroform residue obtained in precisely the same manner had the acrid tobacco odor usually observed in commercial samples of nicotine.

In the examination of organic mixtures for the separation of nicotine it has heretofore been usual for analysts to advise either oxalic, tartaric, or sulphuric acid as the acidifying agent. But we have not found that either of these acids possesses for this purpose any advantage over acetic acid, and, on the whole, prefer the latter. If sulphuric acid be employed, no more should be added than just sufficient to give the mixture a very slight acid reaction. It may here be remarked that anhydrous acetate of nicotine is more or less volatilized by continued heating on a water-bath; and, also, that this salt is soluble to a notable extent in ether.

For the separation of the liquid alkaloids, nicotine and conine, from organic mixtures, the following method, based upon the volatility of these alkaloids, has been proposed. The mixture, acidified with from ten to twenty grains of oxalic or tartaric acid, is treated with about twice its weight of strong alcohol and heated to about 66° C. (150° F.), the cooled liquid strained, the residue washed with alcohol and pressed. The extract thus obtained is concentrated at a gentle heat, the resulting aqueous solution separated by filtration from any insoluble matter present, then rendered alkaline by potassium or sodium hydrate, and distilled to very near dryness in a retort provided with a proper receiver: the residue in the retort may be treated with a little water and again distilled, the product being received with the first distillate. The alkaloid will now be present in the distillate.

This liquid may either be agitated with several volumes of *ether*, the ethereal solution decanted, and the operation repeated with fresh portions of ether until a drop of this fluid upon spontaneous evaporation no longer leaves a residue of the alkaloid; the mixed ethereal liquids are then evaporated spontaneously at a low temperature, and the residue placed for a few moments over sulphuric acid under a glass receiver. Or, the distillate may be neutralized with oxalic acid, concentrated at a low temperature to a small volume, the

residual liquid rendered alkaline by potassium or sodium hydrate, and the alkaloid then extracted by ether. Chloroform might, of course, be substituted for ether in either of these processes.

Since this method, by distillation, is always attended with a quite notable loss of the alkaloid, it is not as well adapted for the detection of very minute quantities of the poison as the method before considered.

Section II.—Conine. (Conium Maculatum.)

History.—*Conine*, known also as *conicine*, *conia*, and *conicina*, is the active principle of *Conium maculatum*, or common hemlock. It exists, in the form of an organic salt, perhaps in all parts of the plant, but is most abundant in the fruit. The relative quantity of the alkaloid present in the plant varies with the growth of the latter: according to Geiger, seventy-two parts of the fresh, green, unripe seeds, or one hundred and eight parts of dry, ripe seeds, yield one part of conine. This alkaloid was first obtained as an impure sulphate by Giseke, in 1827; Geiger, in 1831, obtained it in its pure state, and described some of its properties and effects upon animals. Its effects upon animals were more fully examined, in 1835, by Dr. Christison. Various formulæ have been assigned to conine; but according to Gerhardt it has the composition $C_8H_{15}N$. More recently, however, Prof. A. W. Hofmann, of Berlin, has concluded (*Ber. d. Deut. Chem. Ges.*, 1881, 705) that its composition is $C_8H_{17}N$.

Preparation.—Conine may be obtained, according to Dr. Christison, by exhausting the ripe seeds of hemlock with alcohol, distilling off the alcohol, mixing the residual syrup with an equal volume of water and a little potassium hydrate, distilling the mixture in a chloride of calcium bath, and collecting the distillate in a proper receiver. The conine passes over with the water and yields an aqueous solution of the alkaloid, containing oily drops floating upon its surface. If the conine contains ammonia, this may be removed by placing the mixture in vacuo over sulphuric acid, when the gas will escape in the form of bubbles.

J. Schorm has proposed to exhaust the seeds with water acidulated with acetic acid, and evaporate the extract in a vacuum to the consistence of a syrup. Magnesia is then added to the product, and the whole agitated with ether, which will extract the alkaloid in its pure state. (*Amer. Jour. Pharm.*, July, 1882, 359.)

Some years since (1871), H. Schiff announced that he had succeeded in preparing conine artificially; but subsequent examinations proved that the substance thus produced was merely *isomeric* but not identical with conine.

Conine is a most virulent poison, almost equalling in the activity of its action hydrocyanic acid. As yet there seems to be only a single recorded case of poisoning in the human subject by this substance in its pure state (*Arch. der Pharm.*, Sept. 1861, 257); but poisoning by hemlock is of not unfrequent occurrence. Most of these cases have resulted from the mistaking of hemlock for other plants.

Symptoms.—The symptoms occasioned by hemlock are subject to considerable variation, as may be seen from the following cases. In an instance related by Dr. Haaf, a soldier, having eaten some soup containing hemlock leaves, soon fell asleep: in an hour and a half afterward he was insensible and breathed with difficulty; his pulse was slow and hard; the extremities cold; and the face bluish and distended with blood, like that of a person strangulated. An emetic of tartarized antimony was then administered, but it only produced vain efforts to vomit. He complained of being cold, and soon again lost the power of speech and consciousness, and died in about three hours after taking the poison. (*Orfila's Toxicology*, ii. 537.) In a case quoted by Dr. A. Stillé (*Mat. Med.*, ii. 268), a man, who took ten drachms of an extract of hemlock, experienced great restlessness and anxiety, dropped insensible from his chair, had convulsions, and expired in two hours after taking the dose. Dr. Christison relates a case (*op. cit.*, 657) in which an old woman swallowed two ounces of a strong infusion of hemlock leaves with the same quantity of whiskey, and died *an hour* afterward, comotose and convulsed.

The following case is reported by Dr. J. H. Bennett. (*Edin. Med. and Surg. Jour.*, July, 1845, 169.) A man ate a large quantity of hemlock, believing it to be parsley. He soon afterward lost the power of walking, staggered, and finally fell, but still retained his consciousness and intelligence. In about two hours after taking the poison there was complete paralysis of the upper and lower extremities, with occasional spasmodic movements of the left leg; and the patient had lost the power of sight, deglutition, and speech, but was still sensible: his pulse and breathing were natural. The pupils became fixed, the action of the heart very feeble, and death ensued

in about three hours and a quarter after the poison had been taken. In a case quoted by Dr. Pereira (*Mat. Med.*, ii. 732), an overdose of this plant also produced general paralysis: the under jaw fell, the saliva ran from the mouth, the urine dropped from the bladder, and the contents of the rectum were discharged. The patient continued for nearly an hour in this condition, unable to move or to command the slightest muscular exertion, though all the time perfectly sensible; but under the use of stimulants he finally recovered.

Conine, when administered in its pure state, according to the experiments of Dr. Christison, acts at first as a local irritant; but its local effects are quickly followed by general palsy of the muscles, affecting first those of voluntary motion, then the respiratory muscles of the chest and abdomen, and lastly the diaphragm, ending in death by asphyxia. In some cases convulsive tremors were observed. The heart continued to pulsate after other signs of life had ceased. In no case did the external senses seem to be affected until respiration was impaired. This observer states that a single drop of the alkaloid applied to the eye of a rabbit killed it in nine minutes; and three drops, applied in the same manner, killed a strong cat in a minute and a half. Five drops, introduced into the throat of a small dog, began to act in thirty seconds, and proved fatal in one minute; and two grains of the hydrochloride, injected into the femoral vein of a young dog, killed it before there was time to note the interval. (*On Poisons*, 655.)

The following results were observed in some of our own experiments with the pure alkaloid. A single drop of the alkaloid was placed upon the tongue of a large and healthy cat. In a few seconds the animal was inclined to stand still, and manifested an unsteady gait when disturbed; in two minutes and a half it fell on its right side, then voided urine, had violent convulsive movements of the limbs, and a tremulous motion of all parts of the body, and was dead in three minutes after the poison had been administered. In another experiment, the animal, being immediately placed upon its feet, stood perfectly still, and the pupils of the eyes became dilated and insensible; in forty-five seconds the legs of the animal became powerless, and it sank upon its abdomen, then passed urine, had violent spasms of the extremities, and died in four minutes after the exhibition of the poison.

Treatment.—The treatment in poisoning by hemlock is much

the same as that already pointed out for an overdose of tobacco (*ante*, p. 438). As an emetic, mustard has been strongly advised. Dr. Pereira was of the opinion that strychnine might be found beneficial, on account of its opposite physiological effects to those of conine.

Post-mortem Appearances.—There is generally more or less venous congestion, especially in the brain, and a fluid condition of the blood. In the case reported by Dr. Haaf, the stomach was found half filled with undigested matters, and there were some red spots around the pylorus. The intestines were natural, and the vena cava and heart empty, but all the vessels of the brain were highly gorged with liquid blood. In the case examined by Dr. Christison, in which death took place in an hour, the vessels of the brain were not particularly turgid, but the blood throughout the body was remarkably fluid.

In Dr. Bennett's case, sixty-three hours after death an unusual quantity of fluid blood was found in the vessels of the scalp and in the sinuses of the brain; with slight serous effusion beneath the arachnoid membrane, and into the ventricles, and numerous bloody points in the substance of the brain. The lungs were gorged with dark-red, fluid blood. The blood throughout the body was of a dark color and fluid. The stomach contained a pultaceous vegetable mass; and the mucous membrane was much congested, especially at its cardiac extremity. The intestines and other viscera were healthy, but partially congested. On examining the contents of the stomach, they were found to contain fragments of leaves of the *Conium maculatum*, which on being bruised in a mortar, with a solution of caustic potash, evolved the peculiar mousy odor of conine.

Chemical Properties.

General Chemical Nature.—Conine, in its perfectly pure state, is a colorless, transparent, oily liquid, having a strong alkaline reaction, and, according to Blyth, a specific gravity of 0.87; it has a peculiar, repulsive, and suffocating odor, resembling somewhat that of a long-used tobacco-pipe. When the alkaloid is diluted with water it emits an odor similar to that of mice. This peculiar odor is perceptible even in highly diluted solutions: a few drops of a pure aqueous solution containing only the 1–50,000th of its weight of the free alkaloid, when enclosed for a little time in a

small test-tube, impart the odor, in a very marked degree, to the contained air.

Conine imparts a transient greasy stain to white paper, and burns with a bright, smoky flame; its taste is repulsive and persistent. Its boiling point, according to Th. Wertheim, is 163.5° C. (326° F.); but it distils with the vapor of water at 100° C. (212 F°.), with, however, partial decomposition. The more rapidly it is distilled, the less decomposition it suffers. When heated in an atmosphere of hydrogen gas, it may be distilled without change. When preserved from the action of the air, it remains colorless, but upon exposure it becomes yellow, then brownish, and it is finally resolved into a brownish resin and ammonia.

Solubility.—According to Geiger, with whose observation our own closely agrees, *conine* dissolves at ordinary temperatures in about one hundred parts of pure water; its aqueous solutions, when not too dilute, have a strongly alkaline reaction. When excess of conine is agitated with water, it divides into minute drops and gives the mixture a milky appearance; on repose, the excess of the alkaloid collects on the surface of the water as an oily layer. It is very soluble in alcohol, in ether, and in chloroform. Both ether and chloroform readily separate the alkaloid from its aqueous solutions, and upon spontaneous evaporation leave it in the form of oily drops; the former of these liquids separates conine from water much more readily than it does nicotine.

1. *Extraction by Ether.*—When a 1–100th aqueous solution of free conine is agitated with *five volumes* of ether, and this fluid decanted, the aqueous liquid is reduced to about a 1–4000th solution of the poison. Under these circumstances, therefore, ether extracts about 39-40ths of the alkaloid.

2. *By Chloroform.*—When a 1–100th solution of the free alkaloid is agitated with *five volumes* of chloroform, the aqueous solution is reduced to about the same extent as when treated under similar circumstances with ether.

Special Chemical Properties.—Exposed to the vapors of volatile acids, conine gives rise to dense, white fumes. It neutralizes acids completely, forming odorless salts, but few of which have been obtained in the crystalline state. The conine used in the present investigations was freshly prepared, had a just perceptible yellowish tint, and was perfectly free from ammonia: at least Nessler's test,

which will indicate the presence of ammonia in a few drops of a 1–500,000th solution of the alkali, failed to indicate its presence in a saturated aqueous solution of the alkaloid.

If a drop of the alkaloid be placed in a watch-glass and covered by an inverted watch-glass containing a drop of *hydrochloric acid,* the glasses immediately become filled with dense, white fumes, and the drop of conine very soon solidifies to a mass of beautiful crystalline needles, Plate VI., fig. 4; after a time similar crystals form in the hydrochloric acid drop. When diluted solutions of the alkaloid are exposed to the vapor of hydrochloric acid, they also give rise to white fumes, and the conine solution when concentrated spontaneously deposits crystalline needles of hydrochloride of conine, $C_8H_{15}N,HCl$, or, according to Hofmann, $C_8H_{17}N,HCl$. The same crystals are obtained by neutralizing an aqueous solution of the alkaloid with the diluted acid, and allowing the mixture to evaporate spontaneously. The crystals are permanent in the air: the statement of some writers that they are deliquescent is erroneous.

When strong hydrochloric acid is brought in contact with pure conine, the mixture assumes a pale red color, which increases in intensity, and after a time becomes nearly blood-red; if the mixture be evaporated spontaneously to near dryness, it deposits a mass of long, crystalline needles, which are readily soluble in water and in alcohol, and redeposited as the liquid evaporates.

An aqueous solution of conine, when treated with a saturated solution of *chlorine gas,* becomes turbid. A drop of a 1–100th solution yields in this manner a dense, white turbidity; the same quantity of a 1–1000th solution yields after a time a slight cloudiness.

Nitric acid exposed to the vapor of conine gives rise to dense, white fumes. When the alkaloid is treated directly with excess of the acid, it yields after a little time a pale red mixture, which after a few days becomes converted into a deep red liquid containing a mass of colorless, crystalline needles.

Sulphuric acid forms with the pure alkaloid a pale red liquid, which after a few days deposits crystalline needles along the margin of the mixture. If a sulphuric acid solution of the alkaloid or of any of its salts be treated with a small crystal of potassium dichromate, the mixture upon being stirred slowly assumes a green color, due to the formation of sesquioxide of chromium.

Upon neutralizing pure conine or its aqueous solution with oxalic

acid, the mixture upon spontaneous evaporation yields prismatic crystals of the oxalate of conine. If the mixture be evaporated in a water-bath, the salt is left in the form of a gummy mass.

Most of the *salts* of conine are soluble in water and in alcohol, but nearly or altogether insoluble in ether. When their aqueous solutions are treated with a mineral alkali, the alkaloid is liberated and emits its peculiar odor; from somewhat strong solutions of its salts the alkaloid separates in the form of minute drops, which finally collect upon the surface of the mixture as an oily layer. On distilling an aqueous mixture of a salt of conine and potassium or sodium hydrate, the liberated alkaloid passes over with the distillate. If the distillate be neutralized with oxalic acid, evaporated to dryness, and the residue digested with alcohol, the oxalate of conine will dissolve, while any ammonium oxalate present will remain, it being insoluble in this menstruum.

In the examination of the following tests for conine when in solution, the pure alkaloid was dissolved in distilled water. When a solution of this kind is agitated, it forms a very frothy liquid, even when the mixture contains only the 1–10,000th of its weight of the alkaloid. The fractions indicate the fractional part of a grain of the alkaloid in solution in *one grain* of water. Unless otherwise stated, the results refer to the reactions of *one grain* of the solution.

1. *Auric Chloride.*

A saturated aqueous solution of conine yields with excess of trichloride of gold a copious, bright yellow, amorphous precipitate, which is insoluble in acetic acid and in diluted hydrochloric acid; with a less quantity of reagent the precipitate has a brownish or reddish-brown color. When treated with potassium hydrate, the precipitate assumes a dark color and finally becomes nearly black.

1. $\frac{1}{100}$ grain of conine, in one grain of water, yields a quite copious precipitate.
2. $\frac{1}{500}$ grain: a quite good, yellow deposit.
3. $\frac{1}{1000}$ grain: an immediate cloudiness, and soon a very satisfactory yellow precipitate.
4. $\frac{1}{5000}$ grain gives but little indication of the presence of the alkaloid, even after the mixture has stood for some time.

There was a failure to obtain crystals from any of the foregoing mixtures.

2. *Picric Acid.*

Strong aqueous solutions of conine yield with an alcoholic solution of picric acid a yellow amorphous precipitate, which in a little time changes into microscopic globules, and these after a time deposit large, yellow crystals. The precipitate is insoluble in excess of the reagent, but readily soluble in excess of the alkaloid, and also in acetic acid.

1. $\frac{1}{100}$ grain of conine yields a copious precipitate, which soon becomes crystalline, Plate VI., fig. 5. If the mixture be stirred with a glass rod, it immediately yields streaks of granules and small crystals.
2. $\frac{1}{500}$ grain: an immediate cloudiness, and in a little time a quite good, yellow, amorphous deposit.
3. $\frac{1}{1000}$ grain yields but little indication of the presence of the alkaloid.

3. *Mercuric Chloride.*

This reagent produces in aqueous solutions of conine a white, curdy precipitate, which is but sparingly soluble in water, but readily soluble in acetic and the mineral acids.

1. $\frac{1}{100}$ grain of conine yields a copious, white precipitate, which does not change in color, and remains amorphous.
2. $\frac{1}{500}$ grain yields an immediate turbidity, and soon a good deposit.
3. $\frac{1}{1000}$ grain yields in a few moments a distinct cloudiness, and in a little time the mixture becomes quite turbid.

4. *Iodine in Potassium Iodide.*

A solution of iodine in an aqueous solution of potassium iodide produces in solutions of conine an immediate reddish-brown, amorphous precipitate, which soon turns yellow, then dissolves to a clear solution; upon further addition of the reagent, the precipitate may be reproduced, even several times, from somewhat strong solutions of the alkaloid. If a very large excess of the reagent be at first added, the precipitate is permanent. It is readily soluble in acetic acid.

1. $\frac{1}{100}$ grain of conine yields a very copious precipitate.
2. $\frac{1}{1000}$ grain: a copious deposit.
3. $\frac{1}{10,000}$ grain: a very good, brownish-yellow precipitate.

4. $\frac{1}{25,000}$ grain: a very satisfactory, yellowish deposit.
5. $\frac{1}{50,000}$ grain yields a quite good, yellowish turbidity.
6. $\frac{1}{100,000}$ grain: a distinct turbidity.

5. *Bromine in Bromohydric Acid.*

If a small drop of *anhydrous* conine be placed in a watch-glass, and this covered by an inverted glass containing a drop of an aqueous solution of bromohydric acid saturated with bromine, the glasses become filled with dense, white fumes, and soon crystalline needles form in the conine drop, and this on spontaneous evaporation of the liquid leaves a mass of long, colorless needles; the drop of reagent also leaves on spontaneous evaporation a very good deposit of similar crystals. When an *aqueous* solution of the alkaloid is exposed to the vapor of the reagent, it also evolves white fumes, even when the solution contains only the 1–1000th of its weight of conine.

On treating anhydrous conine directly with the above reagent, it yields a yellow, amorphous mass, which soon becomes converted into large, orange-colored globules; these soon become yellow, and after a time deposit colorless, prismatic crystals. If the mixture be evaporated spontaneously, it leaves a mass of large crystalline needles, which are readily soluble in alcohol, and reproduced as this liquid evaporates. These reactions, however, are modified somewhat by the relative quantities of conine and the reagent present.

When the reagent is added to an aqueous solution of the alkaloid, it produces a yellow, amorphous precipitate, which after a time changes into oil-like globules; upon further addition of the reagent, the yellow amorphous precipitate is reproduced. On allowing the mixture to evaporate spontaneously, it sometimes leaves a crystalline residue, but sometimes only a gummy mass, the result depending upon the relative quantity of reagent present. The precipitate is readily soluble in acids, even in acetic acid.

1. $\frac{1}{100}$ grain of conine, in one grain of water, when exposed to the vapor of the reagent, yields after a time a deposit of crystalline needles; if this mixture be allowed to evaporate, it leaves a mass of similar crystals. When the conine solution is treated directly with the reagent, it yields a copious, yellow precipitate, which soon becomes converted into oily globules. If large excess of the reagent has been avoided, the mixture on spontaneous evaporation leaves a mass of crystals.

2. $\frac{1}{1000}$ grain yields with the reagent a copious, yellow deposit, which soon dissolves, but is reproduced upon further addition of the reagent.
3. $\frac{1}{5000}$ grain: a good, yellowish deposit.
4. $\frac{1}{10,000}$ grain yields a very distinct precipitate, which soon dissolves, and is not reproduced upon further addition of the reagent.

6. *Silver Nitrate.*

When an aqueous solution of conine is treated with a solution of silver nitrate, it yields a brownish precipitate of silver monoxide, which soon becomes converted into the suboxide of the metal, having a nearly black color.

1. $\frac{1}{100}$ grain of conine yields a quite good deposit.
2. $\frac{1}{1000}$ grain: an immediate precipitate, and in a little time a good, flocculent deposit.
3. $\frac{1}{5000}$ grain: a slight cloudiness, and in a little time a quite fair deposit.
4. $\frac{1}{10,000}$ grain: after some minutes the mixture presents a slight cloudiness.

7. *Tannic Acid.*

This reagent produces in aqueous solutions of conine a white, amorphous precipitate, which is readily soluble in a small quantity of hydrochloric acid, but is reproduced upon further addition of the acid, and then is insoluble in large excess. The precipitate is permanently soluble in acetic and nitric acids, as also in excess of the conine solution.

1. $\frac{1}{100}$ grain of conine yields a copious precipitate.
2. $\frac{1}{1000}$ grain: a quite good precipitate.
3. $\frac{1}{10,000}$ grain: the mixture becomes slightly turbid.

Other Reagents.—As conine has strong basic properties, it precipitates the oxides of several of the metals from solutions of their salts. *Mercurous nitrate* produces in strong aqueous solutions of the alkaloid a dirty-brown precipitate, which soon becomes nearly black. One grain of a 1–100th solution of the alkaloid yields a very copious deposit; the same quantity of a 1–1000th solution yields a good, yellowish-white precipitate; and a 1–5000th solution, a dirty-white precipitate. *Lead acetate* produces in a 1–100th solution of the

alkaloid a quite good, white deposit. *Copper sulphate* gives a bluish precipitate, which is insoluble in excess of the conine solution.

A saturated aqueous solution of conine yields no precipitate with either platinic chloride, potassium iodide, potassium chromate or dichromate, potassium ferro- or ferricyanide, or ammonio copper sulphate. Should the alkaloid contain ammonia, as is often the case, it may of course, when treated with platinic chloride, yield a yellow precipitate of the double chloride of platinum and ammonium; but the corresponding salt of conine is freely soluble in water, in which respect this alkaloid differs from ammonia, and also from nicotine. The statement of Orfila, that lead acetate produces no precipitate with conine, is true only of somewhat dilute solutions of the alkaloid.

Fallacies.—An affirmative reaction of none of the above tests for conine in solution, when taken alone, is characteristic of this alkaloid, since each of them produces similar results with solutions of various other substances. But by the concurrent action of two or more of these tests, especially when taken in connection with the odor and physical state of conine, the presence of the alkaloid, even in minute quantity, may be determined with certainty.

Conine and nicotine are distinguished from other alkaloids in being liquid at ordinary temperatures, by their peculiar odor, and in that when their aqueous solutions or solutions of their salts previously mixed with a fixed alkali are distilled, they appear in the distillate and impart to it, at least after concentration, an alkaline reaction. In this connection, however, it must be borne in mind that on distilling a mixture containing ammonia, this alkali will also appear in the distillate and impart to it an alkaline reaction; but this substance is readily distinguished, even by its odor, from the volatile alkaloids.

Conine is distinguished from nicotine: 1. By its peculiar odor, which is characteristic even in highly diluted solutions; 2. Its sparing solubility in water; 3. In yielding crystalline needles when exposed to the vapor of, or treated directly with, hydrochloric acid; 4. By yielding a white precipitate with corrosive sublimate, which remains amorphous and unchanged in color; 5. Its behavior with picric acid; 6. Its behavior with bromine in bromohydric acid; 7. In giving a dark brown precipitate with silver nitrate; and, 8.

By failing to yield a precipitate with platinic chloride. On comparing the special reactions of these alkaloids, as already detailed, other differences will be observed.

A solution of conine may be distinguished from ammonia in the same manner as already pointed out for distinguishing this alkali from nicotine, in the special reactions of the latter.

Separation from Organic Mixtures.

If, in poisoning by hemlock, any solid parts of the plant are found, they may, sometimes, be identified by their botanical characters (see *Pereira's Mat. Med.*, ii. 727), and by their evolving the peculiar odor of conine when moistened with a solution of potassium hydrate and bruised in a mortar.

Conine may be recovered from organic solutions, the contents of the stomach, the tissues, and the blood, in precisely the same manner as already pointed out for the recovery of nicotine. Since most of the salts of conine are not altogether insoluble in ether, if this liquid be employed for the separation of foreign organic matter from an aqueous solution of a salt of this kind, the decanted ether should be reserved for future examination, if necessary.

A fluid-ounce of blood taken from each of the two cats before referred to—each of which was killed by a single drop of conine—was examined after the method pursued in the investigation of the blood from the cats poisoned by nicotine, as already described. The final solution from the blood of both animals, when reduced to three drops and tested by its odor and three different reagents, gave results which, knowing all the circumstances, there is no doubt were due to the presence of conine; yet in an unknown case the results would by no means have justified the assertion that the poison was certainly present. On mixing the 1–100th of a grain of conine with an ounce of normal blood, and pursuing the above method of analysis, the results were equivocal; but when the 1–25th of a grain of the poison was added, the results were quite satisfactory. From a comparison of the special tests for conine and nicotine, it is quite obvious that they will indicate with certainty the presence of a much smaller quantity of the latter than of the former alkaloid.

According to M. Zalewski (*Virchow's Jahresb.*, 1869, i. 365), conine may be found in the blood after every trace has disappeared from the stomach, even when death has supervened very early; and

the poison speedily appears in the urine, and is constantly present in this excretion during the course of the toxic symptoms. According to this observer, the alkaloid is excreted almost entirely through the kidneys, and it was detected in the urine of a dog two and a half days after the administration of the poison.

CHAPTER II.

OPIUM AND SOME OF ITS CONSTITUENTS.

I. Opium.

History and Chemical Nature.—This substance is the concrete juice of the *Papaver somniferum*, or white poppy, and is obtained by making incisions into the capsules when in their unripe state. In regard to its chemical nature opium is extremely complex; and its composition varies somewhat in the several commercial varieties. Thus, besides gum, resin, coloring matter, and inorganic substances, it contains, according to the results of different observers, some fifteen or more crystallizable organic principles, most of which have alkaloidal properties. Of these principles the only ones that will be separately noticed at present are the alkaloids *morphine*, *narcotine*, *codeine*, and *narceine*, the neutral substance *opianyl*, or *meconin*, and the organic acid, *meconic*.

The poisonous properties of opium are due chiefly to the morphine which it contains, which is present principally in combination with meconic acid, as meconate of the alkaloid. Of the several varieties of opium, the Smyrna is usually regarded as containing the greatest proportion of morphine. From the best samples of this variety Merck obtained thirteen per cent. or more of the alkaloid, while from the poorest he obtained only from three to four per cent. On an average, perhaps, opium as found in the shops contains from eight to ten per cent. of morphine. According to the *U. S. Pharmacopœia*, in its normal, moist condition the drug should contain not less than nine per cent. of morphine. Of twenty samples of opium that we examined, the average proportion of morphine was 9.85 per cent., the extremes being 8.41 and 11.29 per cent. of the alkaloid. It is said that certain kinds of opium sometimes contain twenty per cent., and even more, of morphine.

This drug is sometimes taken as a poison in its solid state, but more frequently in the form of *Laudanum*, or *Tincture of opium*, which is an alcoholic solution of the drug. The medicinal dose of *opium* in its solid form for an adult varies, according to circumstances, from half a grain to five grains, the ordinary dose being about one grain; the dose of the *tincture*, under like circumstances, varies from ten minims to one fluid-drachm. According to the last *U. S. Pharmacopœia* (1880), one hundred parts by weight of laudanum should represent the extractive matter of ten parts of dried opium, having a morphine strength of not less than twelve nor more than sixteen per cent. About eleven minims, or twenty-two drops, would, therefore, represent one grain of opium; and a fluid-drachm about 5.4 grains of the dried drug. Laudanum yields about one hundred and twenty *drops* to the fluid-drachm.

Since opium is liable to considerable variation in regard to the proportion of morphine present, and as the strength of the tincture is much influenced by the strength of the spirit used and the period of maceration, and, also, as the tincture itself is sometimes fraudulently diluted, it is obvious that laudanum, as found in the shops, is subject to great variation in quality. Of forty-seven samples of laudanum examined by H. B. Parsons, of New York (*New Remedies*, July, 1883, 194), the amount of morphine ranged from 0.9 grain to 7.4 grains per fluid-ounce, the average being 3.27 grains; the specific gravity from .938 to .966; and the weight per fluid-ounce from 427.8 to 440.5 grains. These samples, however, were collected from distant places before the new *Pharmacopœia* had been issued, and hence should be judged by the standard of the *Pharmacopœia* of 1870. Poisoning by opium has been of more frequent occurrence than perhaps by any other known substance.

Symptoms.—When a poisonous dose of *opium* or of its *tincture* has been swallowed, the patient is sooner or later seized with confusion in the head, giddiness, and stupor; the stupor soon increases in intensity, and eventuates in complete insensibility. In this state the respiration becomes slow; the pulse full, slow, and laboring; the eyes closed; the pupils usually contracted and insensible to light, and the person appears as if in a profound sleep. As the case advances, the countenance becomes pale and ghastly; the lips livid; the skin cold and moistened with perspiration; the breathing slow and stertorous; the pulse feeble and almost imperceptible; the limbs relaxed, and

death in some instances is preceded by convulsions. Convulsions, however, are rarely met with in adults, yet they are not uncommon in children: when they do occur they are often very severe. The pupils, as already stated, are usually contracted, being in some cases nearly closed, yet they are not unfrequently dilated, especially in the advanced stage of the case. The state of the pulse is also liable to considerable variation. In some few cases vomiting, and in other cases purging, has occurred. In fact, a few instances are related in which vomiting was about the only symptom produced by large doses of the drug. In cases of recovery from large doses of the poison, the stupor is often followed by giddiness, headache, nausea, and vomiting.

The *time* within which the symptoms first manifest themselves is somewhat various, depending upon a variety of circumstances, but they are not often delayed beyond an hour. In some instances, especially when the poison is taken in a state of solution and on an empty stomach, its effects appear within a few minutes. Dr. Christison (*op. cit.*, 543) refers to several instances in which the symptoms occurred, in adults, within about ten minutes; in one of these, the sopor was fairly formed in fifteen minutes after two drachms of solid opium had been taken. In a case quoted by Dr. Taylor (*On Poisons*, 588), the patient was totally insensible in fifteen minutes after the poison had been swallowed.

On the other hand, a case is reported in which a woman swallowed about *eight ounces* of solid opium, and in *an hour* afterward was able to tell connectedly all she had done (see *post*). Another instance is related, in which an habitual drunkard took, while intoxicated, two ounces of laudanum, and had no material stupor for *five hours*, during which period vomiting could not be induced. Five hours afterward he was found insensible, and he eventually died under symptoms of opium poisoning. In a case reported by Dr. G. C. Gibb, a healthy man swallowed, with suicidal intent, twelve drachms of laudanum, and no symptoms of poisoning manifested themselves until *nine hours* after the dose had been taken; spontaneous vomiting then occurred, and, under careful treatment, the patient entirely recovered. (*Amer. Jour. Med. Sci.*, Jan. 1858, 288.) In a remarkable instance related by Dr. Christison, a man swallowed an ounce and a half of laudanum, and in an hour afterward half as much more, and no well-marked symptoms appeared until the *eighteenth hour*. The patient then became insensible, and

continued in this condition for several hours; but he eventually recovered.

The *external application* of opium to an ulcerated or abraded surface, and even to the sound skin, has in several instances been followed by serious results. Thus, a child, two months old, nearly perished in consequence of a cerate containing fifteen drops of laudanum having been kept for twenty-four hours on a slight excoriation produced by a fold of the skin. And Sir A. Cooper mentions a case in which a solution of opium applied to an extensive scald on a child proved fatal. In another case, a young man, suffering under some slight ailment, applied a poultice containing a large quantity of laudanum to the sound skin over the pit of the stomach, after which he went to sleep. Symptoms of narcotism soon appeared, and, although the usual treatment was employed, the patient died from the effects of the application. (*Stillé's Mat. Med.*, i. 671.)

The administration of opium in the form of *enema* has also been followed by fatal results. In a case quoted by Dr. Beck, *twelve drops* of laudanum, used as an injection to allay the pain consequent on cauterization for a strictured rectum, produced all the symptoms of narcotic poisoning, and death in seventeen hours. (*Med. Jur.*, ii. 796.) In a case related by Dr. J. B. Jackson, *five drops* of laudanum injected into the rectum of a child eighteen months old caused death in six hours. (*Amer. Jour. Med. Sci.*, Oct. 1854, 384.) In this connection it may be mentioned that Dr. Christison states that he has given by injection one fluid-drachm, and even two drachms, of laudanum without producing any serious symptoms.

Period when Fatal.—The ordinary duration of fatal poisoning by opium, according to the observations of Dr. Christison, is from seven to twelve hours. Several instances, however, are recorded in which death took place with much more than the usual rapidity. In a case quoted by Dr. Beck, a soldier who had taken two ounces and a half of *liquor opii sedativus* was rendered totally insensible in fifteen minutes, and died from its effects in *one hour and twenty* minutes. (*Med. Jur.*, ii. 792.) Dr. G. Lyman reports a case in which an ounce of laudanum, taken by a woman, aged fifty-two years, produced violent symptoms in thirty-five minutes, and death in *three-quarters of an hour*. (*Amer. Jour. Med. Sci.*, Oct. 1854, 383.) And, in the Journal just cited, a case is reported by Dr. Coale, in which death took place within the same brief period. These are

among the most rapidly fatal cases yet recorded. In a case reported by Dr. J. Dawson (*Ohio Med. and Surg. Journ.*, iii. 527), about an ounce of laudanum proved fatal to a strong man in six hours.

On the other hand, cases are related in which death was delayed much beyond the usual period. Thus, several instances are reported in which death did not take place until from fifteen to twenty hours after the poison had been taken. In an instance related by Dr. H. F. Campbell, in which nearly three ounces of laudanum had been swallowed by a young man, aged twenty-eight years, death did not ensue until after twenty hours. (*Amer. Jour. Med. Sci.*, Oct. 1860, 570.) And in a case reported by M. Alibert, death did not occur until the twenty-fourth hour; and in another, mentioned by Dr. Beck, life was prolonged until the forty-eighth hour. The time within which death takes place seems to have but little relation to the quantity of poison taken.

Fatal Quantity.—The smallest quantity of opium that may destroy life cannot be stated with certainty. Dr. Taylor refers to an instance in which ten grains of the solid drug proved fatal to a man; and another, in which eight grains destroyed the life of a woman. (*On Poisons*, 598.) And Dr. Christison mentions a case in which *four grains and a half*, mixed with nine grains of camphor taken by an adult, was followed by the usual symptoms of narcotism, and death in nine hours. In a case reported by Dr. Morland (*Amer. Jour. Med. Sci.*, Oct. 1854), five grains of solid opium, taken in mistake by a gentleman, produced all the usual symptoms of the drug, and the patient barely escaped with his life. In another case, thirty grains of the drug caused death in eleven hours.

A case has already been cited in which an ounce of laudanum proved fatal to an adult in three-quarters of an hour. And in another instance, reported by Dr. W. F. Norris (*Amer. Jour. Med. Sci.*, Oct. 1862, 397), a similar quantity caused the death of a healthy man in about eighteen hours, although the most active remedies were employed. In a case for the details of which I am indebted to Dr. R. M. Denig, a robust, healthy girl, aged seventeen years, in a fit of despondency, swallowed *two drachms* by measure of laudanum. In about three hours afterward she was seized with stupor, and died under the usual symptoms of narcotic poisoning in about seven hours after the dose had been taken. The respectable druggist who prepared and sold her the laudanum testified that at most it contained

the soluble portion of only seven grains of opium. Dr. Toogood relates an instance in which twelve drops of "Battley's sedative,"—which is usually regarded as having about three times the strength of ordinary laudanum,—taken by a feeble woman, aged fifty-five years, produced the usual symptoms of opium poisoning, and death on the following day. (*Provincial Med. and Surg. Jour.*, Nov. 1841, 129.)

Numerous instances are recorded in which extremely small quantities of opium proved fatal to very young children. In a case that fell under our own observation, three drops of laudanum caused the death of a child two weeks old in about six hours. In a case mentioned by Dr. Beck, two drops of laudanum, given four times during a period of eighteen hours, proved fatal to a child six weeks old. Even a single dose of two drops of laudanum caused the death of an infant four days old; and in another instance, an infant six days old was killed by a *single drop* of the opiate preparation. Dr. Schaefer reports an instance in which three-quarters of a grain of solid opium taken in two doses, one-half the quantity being administered five hours, and the remainder three hours, before death, proved fatal to a child. In a recent instance (*Med. Times*, Jan. 1880, 165), about two and a half grains of the drug caused the death of a child, nineteen months old, in nine and a half hours.

Notwithstanding these facts, recovery has not unfrequently taken place after very large quantities of the drug had been taken. In a case reported by Dr. J. B. Jackson, a woman swallowed ninety grains of solid opium, and was not seen by a physician until three hours after the occurrence. She was then laboring under all the symptoms of opium poisoning; yet, under active treatment, she eventually recovered. (*Amer. Jour. Med. Sci.*, Oct. 1854, 385.) In another case, a stout, muscular woman, who, under disguise, had served several months as a common soldier in the late war, took for the purpose of self-destruction sixty grains of solid opium; in about two hours afterward, being disappointed in the effects of the drug, she swallowed half an ounce of laudanum, and about half an hour later took as much more. When seen, about three hours and a half after taking the first dose, by Dr. J. B. Thompson, to whom I am indebted for the particulars of the case, she was perfectly rational, and told all she had done. Emetics of sulphate of zinc and ipecacuanha were then administered, but they did not operate until after about half an hour, when they brought away a large mass of matter having a strong

opiate odor; the vomiting was kept up for about three-quarters of an hour. She at no time suffered severe narcotism, was soon out of danger, and rapidly recovered. From several circumstances connected with this case, there is no doubt that the patient took the quantities of opium and laudanum stated, which are equal to nearly one hundred grains of the crude drug.

One of the most remarkable cases of this kind yet recorded is the following. A pregnant woman, aged thirty-two years, took, with suicidal intent, between seven and eight *ounces* of solid opium. When seen by a physician in about an hour afterward, she was able to relate in a connected manner the history of her case. The administration of an emetic caused copious vomiting, by which lumps of opium of the size of hazelnuts were ejected. The emetic was repeated, and its operation encouraged by large draughts of warm water: it was presumed that this vomiting brought away at least three ounces more of opium. The patient then fell into a deep sleep, from which she could with difficulty be roused; but at length she became more sensible, and complained of violent burning pain in the stomach. After a little time a reaction took place, and symptoms of phrenitis manifested themselves; but she finally recovered. (*American Medical Recorder*, xiii. 418.)

Treatment.—In poisoning by opium or any of its preparations, any portion of the unabsorbed poison should be quickly removed from the stomach. For this purpose the stomach-pump will usually be found the most efficient; but in the absence of this instrument an emetic of from twenty to thirty grains of sulphate of zinc or about ten grains of sulphate of copper should be exhibited. If neither of these emetics be at hand, powdered mustard or a solution of common salt should be freely administered. If symptoms of narcotism have already manifested themselves, an emetic may fail to act. Under these circumstances, therefore, great caution should be exercised in the administration of any of the more poisonous emetics, such as the sulphate of copper and tartar emetic.

For the purpose of producing emesis in cases of this kind, Dr. A. Routh advises (*London Lancet*, April, 1883, 316) a two per cent. solution of *apomorphia*, administered subcutaneously in doses of from three to ten minims. This will usually cause emesis in from two to five minutes, the contents of the stomach being generally voided in one rush without previous nausea.

During the progress of the case it is of the utmost importance that the patient be kept constantly roused. For this purpose various methods have been advised, such as keeping the patient in continual motion, flagellations with wet cloths, and the dashing of cold water over the head and chest. Sometimes the dashing of cold water over the patient insures the operation of an emetic. One of the most efficient methods yet proposed for preventing a state of insensibility or for rousing the individual from this condition is a current of magneto-electricity applied to the spine and chest. Many cases are reported in which this method was employed with complete success; and we have in two instances used it with similar results. (*Ohio Med. and Surg. Jour.*, May, 1858, 388.) As a stimulant, a strong decoction of coffee has been highly recommended; in fact, several instances are reported in which it is claimed that a decoction of this kind was the means of saving life. In extreme cases artificial respiration has been employed with great advantage.

As a chemical antidote, Orfila advised the free administration of vegetable solutions containing tannic acid, on the ground that this acid forms with the active principle of opium a compound only sparingly soluble in water. So, also, solutions of iodine and of bromine have been strongly recommended. In practice, however, these substances have been found of little service. Various other chemical antidotes have been proposed; but the utility of these seems to be even more doubtful than that of the substances already mentioned.

From the antagonistic action, whether apparent or real, existing between the physiological effects of opium and those of belladonna (or its active principle atropine), it was long since claimed that these substances are mutually antidotal to each other; and within late years numerous instances have been reported which seem to leave no doubt whatever as to the reciprocal antidotal action of these substances.

A case of this kind, in which it is believed that three ounces of laudanum had been taken, is related by Dr. H. J. Horton. (*Med. and Surg. Reporter*, Philadelphia, Sept. 1866, 225.) Out of nine cases of opium poisoning treated by belladonna, and eighteen of belladonna poisoning treated by opium, collected by Dr. W. Norris, of Philadelphia, only two of the former and one of the latter proved fatal. (*Amer. Jour. Med. Sci.*, Oct. 1862, 395.) Of eleven cases

of opium poisoning treated by the hypodermic injection of atropine, by D. J. Johnston, of Shanghai, all the patients recovered. (*Med.-Chir. Rev.*, Jan. 1873, 248.)

Post-mortem Appearances.—The most common morbid appearances after death from poisoning by this substance are turgescence of the blood-vessels of the brain, effusion between the membranes and into the ventricles of this organ, a congested state of the lungs, and general fluidity of the blood. But these appearances are by no means constant, nor are they peculiar to death from opium. In some few instances the mucous membrane of the stomach has presented a reddened appearance; but not, perhaps, as the direct result of the action of the poison. When the poison has been taken in its crude state or in the form of laudanum, the contents of the stomach not unfrequently evolve the peculiar odor of opium; but even this character is often wanting, the poison having disappeared from the stomach prior to death.

In a case related by Dr. C. A. Lee, in which a large quantity of laudanum had been taken and death did not occur until the sixteenth hour, the superficial veins of the scalp were found very full of dark, uncoagulated blood. The longitudinal and lateral sinuses of the brain were distended with blood; and between the pia mater and arachnoid membrane there was a large collection of serum, of a yellowish hue. The choroid plexus was very vascular, and in the bottom of the ventricles there were small flakes of purulent matter. The lungs were congested; and the right side of the heart was full of coagulated blood. The mucous villi of the cardiac orifice of the stomach were redder than natural and much softened. The termination of the œsophagus seemed inflamed, and the mucous lining of the intestines erythematous. (*New York Med. and Phys. Jour.*, xxx. 297.)

In Dr. Dawson's case, in which death occurred in six hours, the body and limbs presented a bluish appearance, and, although the inspection was made while the body was still warm, the limbs were stiff and unyielding. The membranes of the brain were found congested, and the arteries, veins, and sinuses were filled with dark blood. The lungs appeared natural; when cut, dark blood flowed freely from the vessels. The liver was healthy. The mucous membrane of the stomach around the cardiac and pyloric orifices was in a state of hyperæmia, being most intense and extensive about the former.

In a case reported by Dr. Ogle (*St. George's Hosp. Rep.*, 1868, 224), the contents of the cranium were natural, there being no extensive congestion or effusion of fluid found in the cavities or membranes. In the case observed by Dr. Schaefer, there was a spongy condition of the lungs, which were gorged with black, fluid blood; hyperæmia of the liver and spleen, and a full urinary bladder. The vessels of the brain were filled with dark, fluid blood; and the ventricles contained a large quantity of effused serum, and several drachms of a similar fluid were found at the base of the brain.

Physical and Chemical Properties.—Opium, in its solid state, has a reddish-brown color, a well-marked and peculiar odor, and a bitter, acrid taste. The odor of this drug readily serves to distinguish it from all other substances except lactucarium, which has a somewhat similar odor. When fresh, opium is quite soft and plastic, but on exposure to the air it slowly becomes hard and brittle, and is then readily reduced to a yellowish-brown powder. When moderately heated, it melts to a semi-fluid mass, which readily takes fire, burning with a bright flame. It is somewhat heavier than water, its density being about 1.32. *Laudanum*, or the alcoholic solution of opium, as found in the shops, has a deep brownish-red color, and the odor and taste of the solid drug. The active properties of opium are also taken up by water, when the drug is digested in this liquid; this extraction is much facilitated by a moderate heat, and also by the presence of a free acid. Chloroform and ether, in their pure state, fail to withdraw the active principles of the drug.

Since, as already pointed out, opium consists of a number of different substances, it is obvious that there can be no single chemical reagent that will show its presence as a whole; but this may be inferred by proving the presence of one or more of the substances peculiar to it. Although opium contains several such substances, the ones usually sought for, in medico-legal investigations, are *morphine* and *meconic acid*. Since morphine, as well as several of its salts, is frequently administered or taken alone, it is obvious that proof of the presence of this alkaloid alone would not in all cases justify the inference that opium was present. This deficiency, however, is always supplied when the presence of meconic acid has been established.

Before considering the methods by which morphine and meconic

acid may be separated from complex organic mixtures of the crude drug, the special properties of these substances will be described. The chemical properties of some of the other principles peculiar to opium will then be considered.

II. Morphine.

History and preparation.—Morphine, as found in nature, occurs only in opium, in which it exists chiefly in combination with meconic acid, but partly with sulphuric acid. This alkaloid was discovered, in 1804, by Sertürner; its composition, according to Laurent, is $C_{17}H_{19}NO_3,H_2O$; molecular weight 303.

Morphine may be obtained, according to the method of Gregory, by treating a concentrated aqueous solution of opium with slight excess of a solution of calcium chloride. After a little time, especially if warmed, the mixture deposits a copious precipitate, consisting of a mixture of meconate and calcium sulphate, while hydrochloride of morphine remains in solution. The liquid is then filtered, and the highly colored filtrate concentrated to the consistency of a thin syrup, when, on cooling, the hydrochloride of morphine separates in its crystalline state, forming a nearly solid mass. This is strongly pressed in muslin, redissolved in a small quantity of hot water, the solution filtered, and the salt allowed to recrystallize; this operation is repeated a second and, if necessary, a third time, using a little prepared animal charcoal to absorb the coloring matter. The salt is now dissolved in hot water, and the solution slightly supersaturated with ammonia, when, on standing, the liberated alkaloid is deposited in snow-white crystals.

Various methods have been proposed for the quantitative determination of the morphine present in crude opium. Of several of these that we have examined, that advised by E. F. Teschemacher (*Chem. News*, Feb. 1877, 47), although somewhat tedious, gave the most satisfactory results, especially in regard to freedom from color and the purity of the final product.

Symptoms.—Considerable difference of opinion has existed as to whether or not the effects of morphine and its salts were identical with those occasioned by opium; but, on the whole, the symptoms are much the same, only that the effects of the saline combinations of the alkaloid usually manifest themselves more promptly than in

the case of the crude drug. In addition to the usual narcotic symptoms, itching of the skin, impaired or total loss of vision, and inability to void urine, have frequently been observed. Great lividity of the skin has also frequently been present. The relative strength of morphine and its salts is generally estimated to be about five or six times that of the crude drug.

In a case reported by Dr. Houston, ten grains of the sulphate of morphine, given by mistake to a gentleman, aged fifty-nine years, who was laboring under intermittent fever, caused death in less than two hours, although various remedies were employed. Deep stertorous breathing was the only symptom observed. (*Beck's Med. Jur.*, ii. 799.) Dr. Christison mentions an instance in which a girl, who had taken ten grains of the hydrochloride, was seized with narcotic symptoms within fifteen minutes afterward, and died from its effects in twelve hours. (*Op. cit.*, 558.) In a case reported by Prof. C. Shepard (*Pamphlet*, 1879), seven and a half grains of the sulphate caused the death of a man in less than two hours. Dr. Ebertz relates a case in which something less than four grains of the hydrochloride, taken by a woman in mistake for quinine, proved fatal in fifty minutes. (*Ann. d'Hyg.*, July, 1875, 220.) And in a case reported by Dr. D. W. Prentiss (*Amer. Jour. Med. Sci.*, April, 1867, 562), two pills, containing about three grains of the alkaloid, caused the death of a young mulatto, aged sixteen, in twelve hours.

In a case quoted by Wharton and Stillé (*Med. Jur.*, 581), a gentleman affected with acute rheumatism died from the effects of one grain and a third of morphine, taken in four pills at intervals of an hour between each. One grain of the acetate administered by mistake to a debilitated woman caused her death in about eleven hours. And in another instance, one grain of the hydrochloride, taken in divided doses over a period of six hours, proved fatal to a girl nineteen years old. In a case reported by Dr. Toogood, seven drops of a solution of the acetate of morphine (strength not stated) destroyed the life of an aged woman, under the usual narcotic symptoms, in about twelve hours. (*Provincial Med. and Surg. Jour.*, Nov. 1841, 129.) A solution containing only the twelfth part of a grain of morphine, administered by mistake, caused the death of an infant. (*Chemical News*, London, Aug. 1863, 98.)

On the other hand, Mr. Winterbotham reports a case in which a child, two years and three months old, swallowed one grain of the

acetate of morphine in solution, and the poison remained undisturbed in the system for two hours and a half. At the end of this period, free vomiting was induced by an emetic of sulphate of zinc; and under the use of the ordinary remedies the child entirely recovered. (*Amer. Jour. Med. Sci.*, April, 1863, 520.) In a case related by Orfila, a young man entirely recovered within three days, after having taken, with suicidal intent, twenty grains of the hydrochloride of morphine. Within ten minutes after taking the poison, the patient experienced a sense of heat in the stomach, with intense itching of the skin; but over four hours elapsed before symptoms of stupor manifested themselves. Profound insensibility then supervened, and he was affected with trismus; the pupils became slightly dilated; the surface of the body cold; the pulse rapid; the breathing hurried and stertorous; the abdomen tense and tympanitic, and there were occasional convulsions; and afterward he had difficult and scanty micturition, with pain in the kidneys and bladder, and difficulty of swallowing.

A somewhat similar case to that just mentioned is cited by Dr. Christison, in which a young man swallowed fifty grains of the acetate of morphine, and although he was seized within fifteen minutes with the usual narcotic symptoms of the poison in an aggravated degree, and vomiting could not be induced until four hours afterward, he finally recovered. In a case reported by Dr. Wood (*Boston Med. and Surg. Jour.*, July, 1876, 82), about sixty grains of the acetate had been taken, and the patient finally recovered, although no treatment was employed until four hours after the poison had been taken.

One of the most remarkable cases of recovery yet reported is the following, related by Dr. W. F. Norris (*Amer. Jour. Med. Sci.*, Oct. 1862, 395). A druggist, aged nineteen years, for the purpose of self-destruction, swallowed *seventy-five grains* of the sulphate of morphine. No marked symptoms appeared for an hour and a half afterward, when he began to feel sleepy and had a staggering gait. Soon after this emetics were given, with the effect of producing free emesis. The patient then became unconscious, the pupils contracted to the size of a pin's point, the pulse soft and frequent, and the respiration slow and labored; but under the active use of remedies, including extract of belladonna, the cold douche, and galvanism, he was quite well on the second day after the occurrence.

A case is reported by Dr. Du Bois (*Western Lancet*, June, 1872) in which recovery took place, under active treatment, including large doses of belladonna, after *eighty* grains of the sulphate of morphine had been taken in two doses; and Dr. Chisolm relates another (*Maryland Med. Jour.*, June, 1878), in which one hundred and twenty grains of the salt had been taken at a single dose, and the patient recovered.

The *external application* of morphine to abraded surfaces, as well as its use in the form of enema, has in several instances been followed by serious and even fatal results. A quantity of the alkaloid, perhaps about one grain, applied to a blistered surface on the back of the neck of an aged lady, produced, in the course of about two hours, convulsive agitations, cold sweats, extreme prostration, and threatened suffocation, from which the patient, under active treatment, only slowly recovered. (*American Medical Intelligencer*, ii. 13.) In a case quoted by Dr. A. Stillé (*Mat. Med.*, i. 676), a lady affected with cancer of the uterus was dangerously narcotized by less than one-sixteenth of a grain of hydrochloride of morphine applied to the denuded skin of the epigastrium. Even the one-thirty-second of a grain of the alkaloid applied in this manner has produced very serious symptoms.

An *enema* containing ten grains of sulphate of morphine, prescribed in mistake for quinine, was administered to a child five years old, who was laboring under intermittent fever. Within ten minutes the child became sleepy, and shortly afterward it was seized with violent convulsions; various remedies were now employed, but death speedily ensued. (*Med.-Chir. Rev.*, xv. 551.) In another instance, reported by Dr. Anstie, three grains of the alkaloid given inadvertently as an injection caused death in about sixteen hours. (*Amer. Jour. Med. Sci.*, April, 1863, 520.) The age of the patient in this case is not stated; but it would seem that the person was an adult.

Administered *hypodermically*, even in only minute quantity, morphine has in several instances produced very unexpected results. Thus, an instance is related in which half a grain, employed in this manner for the relief of sciatica, proved fatal to a woman, aged fifty years. So, also, a case is reported in which one-third of a grain produced profound stupor; and another (*Boston Med. and Surg. Jour.*, Oct. 1879, 619), in which about one-eighth of a grain of the sulphate caused most singular and alarming symptoms.

The *Treatment* in poisoning by morphine or any of its salts is the same as that for opium poisoning, already considered.

Post-mortem Appearances.—These are the same in kind as found in poisoning by opium. In a case reported by Dr. J. Dawson (*Ohio Med. and Surg. Jour.*, iii. 525), in which a young woman, with suicidal intent, took about fifty grains of morphine, and died from its effects in forty-eight hours, seventeen hours after death the arteries, veins, and sinuses of the brain were found engorged with black, fluid blood; and the ventricles contained about a drachm of colored serum. The lungs were normal in appearance; the ventricles of the heart contained black blood, the right being the fullest. The mucous membrane of the stomach, for about one-third of its surface, was hyperæmic, especially about the cardiac orifice.

In the case reported by Dr. Prentiss, already cited, there was found congestion of the brain, the blood was quite fluid, and a fibrinous clot was found in the longitudinal sinus; there was no fluid in the ventricles nor in the cavity of the arachnoid. The abdominal organs were all normal in appearance. The cavity of the thorax was not examined.

Chemical Properties.

General Chemical Nature.—Morphine in its pure state crystallizes in the form of short, colorless, odorless, rectangular prisms, which contain one molecule of water of crystallization, $C_{17}H_{19}NO_3$, H_2O. The exact forms of these crystals, however, are subject to considerable variation, depending somewhat upon the method employed for their preparation and the strength of the solution from which they were separated, and even upon the quantity of the solution employed. When gently heated, the crystals part with their water of crystallization and become opaque; at a little higher temperature, they fuse to a brownish liquid, which, if the heat be increased, evolves dense, white fumes, then turns black, and is finally consumed. Morphine has a very bitter taste and strong basic properties. It completely neutralizes diluted acids, forming salts, most of which are crystallizable. It is readily decomposed by concentrated nitric acid and by hot sulphuric acid; but not by the cold caustic alkalies.

Solubility. 1. *In Water.*—When excess of pure, powdered morphine is frequently agitated for twelve hours with water at the ordi-

nary temperature, and the solution then filtered, the filtrate leaves on spontaneous evaporation a crystalline residue indicating that the alkaloid requires about 4166 times its weight of water for solution. It is much more freely soluble in hot water.

2. *In Chloroform.*—Under the conditions just stated, one part of morphine requires about 6550 parts by weight of this fluid for solution.

3. *Ether.*—Under similar conditions, one part of the alkaloid requires 7725 parts of *absolute ether* for solution. *Commercial ether* of specific gravity 0.733 dissolved one part of the alkaloid in 4225 parts of the liquid.

If an aqueous solution of a salt of morphine be decomposed with slight excess of sodium carbonate, and the mixture allowed to repose for a little time, so that the liberated alkaloid may deposit in its crystalline state, and the whole be then agitated with a large quantity of absolute ether, this liquid will take up only a mere trace of the alkaloid, the proportion being even much less than that stated above. If, however, *immediately* after the addition of the sodium carbonate, the mixture be agitated with ether, this fluid will dissolve a much larger proportion of the alkaloid than above stated: under these conditions, one part of morphine was taken up by 2500 parts of absolute ether.

4. *Alcohol.*—When excess of finely-pulverized morphine is digested, with frequent agitation, for ten hours in alcohol of 98 per cent., the filtered liquid leaves on spontaneous evaporation a crystalline residue indicating that one part of the alkaloid had dissolved in 148 parts of the liquid. It is still more freely soluble in hot alcohol; but on cooling, the liquid deposits the greater part of the excess in its crystalline state. A cold, saturated, alcoholic solution of the alkaloid has a well-marked alkaline reaction.

5. *Alcoholic-ether.*—When twenty-five fluid-grains of an aqueous solution containing 10–100ths of a grain of morphine in the form of acetate are treated with slight excess of sodium carbonate, and the whole violently agitated with *five volumes* of a mixture consisting of two parts of absolute ether and one part of pure alcohol, this mixture takes up 9–100ths of a grain of the liberated alkaloid, which on spontaneous evaporation it leaves in the form of brilliant crystals. When a mixture of this kind is agitated, in the proportions just mentioned, the alcoholic-ether takes up about one-third of the

aqueous liquid, the original volume of the latter being reduced to about two-thirds.

6. *Amyl Alcohol.*—When excess of the powdered alkaloid is digested in pure amyl alcohol, with frequent agitation, for four hours at the ordinary temperature, one part is taken up by 133 parts of the menstruum.

On decomposing twenty-five grain-measures of an aqueous solution containing 10–100ths of a grain of morphine as acetate with sodium carbonate, and agitating the mixture with two volumes and a half of amyl alcohol, this liquid extracted the whole of the alkaloid, except the 1–200th of a grain.

7. *Pure Acetic Ether*, when kept in contact with large excess of powdered morphine for several hours, at the ordinary temperature and with frequent agitation, dissolves one part in 1030 parts of the liquid. On allowing the solution to evaporate spontaneously, the alkaloid is left in its crystalline state. In commercial acetic ether, which usually contains alcohol and more or less free acetic acid, the alkaloid is much more freely soluble, even, sometimes, to the extent of one part in 75 parts of the fluid.

When half a grain of morphine, in the form of sulphate, was dissolved in fifty grains of pure water, the solution rendered slightly alkaline by sodium carbonate, and the mixture thoroughly agitated with *three volumes* of pure acetic ether, in two separate portions, this liquid extracted only 0.08 of a grain of the liberated alkaloid.

The alkaloid is readily soluble in solutions of the fixed caustic alkalies; but only sparingly soluble in diluted aqua ammoniæ.

The *salts* of morphine, for the most part, are readily soluble in water, especially if the liquid be slightly acidulated; they are also soluble in diluted alcohol, but *insoluble* in chloroform, ether, amyl alcohol, and pure acetic ether: they are, therefore, not extracted from their aqueous solutions by either of the four last-named liquids. Their aqueous solutions, when pure, are colorless, and have the bitter taste of the alkaloid.

According to D. B. Dott, the following-named *salts of morphine* are soluble in the following proportions respectively of *water*, at a temperature of 15.5° C. (60° F.): morphine hydrochloride, $C_{17}H_{19}NO_3,HCl,3H_2O$, in 23.9 parts; morphine sulphate, $2C_{17}H_{19}NO_3;H_2SO_4,5H_2O$, in 23.01 parts; morphine acetate, $C_{17}H_{19}NO_3,C_2H_4O_2,3H_2O$, 2.44 parts; morphine tartrate, $2C_{17}H_{19}NO_3;C_4H_6O_6,3H_2O$,

9.7 parts; morphine meconate, $2C_{17}H_{19}NO_3$; $C_7H_4O_7,5H_2O$, in 33.9 parts. (*Amer. Jour. Pharm.*, Feb. 1883, 99.)

Special Chemical Properties.—If a few crystals of pure morphine be added to a drop or two of concentrated *sulphuric acid*, they slowly dissolve without change of color, or at most yield a faint pinkish solution. If a crystal of potassium dichromate be now stirred in the solution, it *slowly* yields green oxide of chromium, even if only the 1–100th of a grain of morphine be present. If to the sulphuric acid solution of the alkaloid a drop of potassium dichromate solution be added, the stirred mixture *immediately* acquires a green coloration, even when only 1–1000th grain of the alkaloid is present. If a crystal of *potassium nitrate* be stirred in a sulphuric acid solution of morphine, the mixture assumes a dark brown color.

When a little of the alkaloid or any of its salts is dissolved by the aid of heat in a small quantity of concentrated sulphuric acid, and the solution, after cooling, diluted with a little water, and then a crystal of *potassium chromate* added, the liquid acquires an intensely mahogany-brown color (Otto). Under this treatment the merest fragment of morphine will yield a very satisfactory coloration.

Concentrated *nitric acid* causes the alkaloid to assume a beautiful orange-red color, and dissolves it, with the evolution of nitrogen dioxide (N_2O_2), to a solution of the same hue, which slowly fades to yellow. (See *post.*) The color of the nitric acid solution is not affected by chloride of tin. *Hydrochloric acid* slowly dissolves the alkaloid without change of color.

In the following investigations in regard to the reactions of morphine when in solution, pure aqueous solutions of both the sulphate and the acetate were employed. The fractions indicate the fractional part of a grain of *anhydrous morphine* in solution in one grain of the liquid. When not otherwise stated, the results refer to the reaction of *one grain* of the solution.

1. *Potassium and Sodium Hydrates.*

The fixed caustic alkalies, when added in limited quantity, throw down from concentrated neutral solutions of salts of morphine a white, amorphous precipitate of the anhydrous alkaloid, which in a little time, appropriating a molecule of water, becomes crystalline. From more dilute solutions the precipitate does not appear until after some time, and it then separates in its crystalline form. From

such solutions the formation of the precipitate is much hastened by stirring the mixture with a glass rod. The precipitate is readily soluble in excess of the precipitant, and in free acids, even acetic acid; its nitric acid solution has an orange-red color.

1. $\frac{1}{100}$ grain of morphine in one grain of water yields with a small drop of the reagent, after a few moments, a crystalline precipitate, which in a little time increases to a quite copious deposit, Plate VI., fig. 6. If on the addition of the reagent the mixture be stirred with a glass rod, it immediately yields streaks of crystals along the path of the rod, over the bottom of the watch-glass containing the mixture, and in a few moments there is a very copious crystalline deposit. Since the precipitate is readily soluble in the fixed caustic alkalies, care should be taken to avoid the addition of much excess of the reagent, otherwise no deposit will form.
2. $\frac{1}{500}$ grain yields after a little time, by stirring the mixture, a very good deposit.
3. $\frac{1}{1000}$ grain: when the least possible quantity of reagent is employed, the mixture yields after a time a quite satisfactory granular precipitate.

These reagents also produce in solutions of most of the other alkaloids white, crystalline precipitates; but the crystalline form of the morphine deposit, when from not too dilute solutions, is somewhat peculiar. Its true nature may be fully established by its behavior with nitric acid or some of the other tests mentioned hereafter.

2. *Ammonia.*

Ammonia produces with neutral solutions of salts of morphine much the same results as the fixed caustic alkalies; but the precipitate is not so readily soluble in excess of the precipitant. From dilute solutions, therefore, it is much more easy to obtain precipitates by this reagent than by either potassium or sodium hydrate. If a drop of a solution of the alkaloid be exposed to the vapor of a drop of ammonia suspended on a glass rod, it yields after a little time a white, crystalline deposit. This is much the best method for obtaining precipitates from very dilute solutions of the alkaloid.

The *alkali carbonates*, also, throw down from normal solutions of salts of morphine a white precipitate of the alkaloid, which is only very sparingly soluble in large excess of the precipitant. If, how-

ever, large excess of the reagent be added at first, the formation of the precipitate is partially or entirely prevented. The limit of the reaction of these reagents is the same as that of the caustic alkalies.

3. *Nitric Acid.*

When somewhat strong solutions of salts of morphine are treated with large excess of concentrated nitric acid, the mixture slowly acquires a lemon-yellow or orange-red color, its exact tint depending upon the relative proportion of acid and morphine present.

1. $\frac{1}{100}$ grain of morphine, in one grain of water, yields, with a few drops of the acid, a yellow solution, which very soon acquires an orange color, then a deep orange-red, after which the liquid slowly becomes again yellow.
2. $\frac{1}{1000}$ grain: the mixture slowly acquires a lemon color, which after some minutes becomes light orange.
3. $\frac{1}{2500}$ grain: after some minutes the mixture assumes a quite perceptible lemon hue, which is best seen over a white ground.

The reaction of this test is much more satisfactory and delicate when a small portion of the acid is applied to the alkaloid, or to any of its salts in the *dry* state.

1. $\frac{1}{100}$ grain of morphine—in the form of sulphate or acetate, as left upon evaporating one grain of its aqueous solution to dryness—when touched with a small drop of nitric acid, almost immediately assumes a fine orange-red color, and dissolves to a solution of the same hue, which slowly fades to yellow.
2. $\frac{1}{1000}$ grain: at first the deposit assumes a yellow color, which, however, soon changes to a bright brownish-orange, and dissolves to a fine orange solution.
3. $\frac{1}{6000}$ grain: the residue assumes a very distinct brown color, and dissolves to a faint brownish solution.
4. $\frac{1}{10,000}$ grain, when touched with a very minute quantity of the acid, after a little time acquires a very faint brownish hue.

Brucine, and strychnine containing this alkaloid, immediately strike a deep blood-red or bright red color when treated with strong nitric acid. This color, however, upon the addition of a solution of tannous chloride, is changed to bright purple; whereas that produced from morphine is unaffected, or, at most, is changed to yellow, by this reagent. Nitric acid also produces a more or less red coloration with certain volatile oils and resinous substances, but

none of these are crystallizable, in which respect they differ from morphine.

4. *Iodic Acid.*

When a tolerably strong solution of a salt of morphine, or the alkaloid or any of its salts in the dry state, is treated with a strong solution of iodic acid, the latter is decomposed, with the elimination of free iodine, which falls as a brown or reddish-brown precipitate, and the mixture emits the odor of iodine. If a freshly prepared solution of starch-paste be now added, the mixture acquires a blue color, due to the formation of iodide of starch. For the production of this blue color, however, it is necessary, as pointed out by M. Dupré (*Chemical News*, Dec. 1863, 267), that the proportions of iodic acid and starch employed be within certain limits, since the color is destroyed by large excess of iodic acid, and also by large excess of the starch solution.

1. $\frac{1}{100}$ grain of morphine, in one grain of water, when treated in the above manner, yields a blue precipitate and imparts a deep blue color to the liquid.
2. $\frac{1}{500}$ grain yields a brownish liquid, and a quite distinct blue precipitate.
3. $\frac{1}{1000}$ grain: the mixture assumes a slight brownish color, but it fails to yield a precipitate.

This reaction is much more delicate when applied to morphine or any of its salts in the solid state. For this purpose, as advised by M. Dupré, the morphine or its solution is first treated with a drop of starch solution; the mixture is then carefully evaporated to dryness, and the residue, after cooling, moistened with a solution of iodic acid. In this manner a residue containing only the 1–10,000th of a grain of the alkaloid will yield a quite distinct blue color.

The reactions of this test are common to many other substances, some of which, like morphine, are crystallizable.

M. Lefort has recommended to treat the mixture of morphine and iodic acid with ammonia instead of starch, by which the yellow color of the mixture is changed to deep brown or yellowish-brown. In applying this method to dilute solutions of the alkaloid, the iodic acid mixture should be allowed to stand some minutes before the ammonia is added, since otherwise the coloration may be entirely prevented.

This method, when applied to solutions, is much more delicate than the starch process before described; and, moreover, it is said that the yellow color produced by iodic acid with most other substances capable of reducing this acid is discharged by ammonia, whereby morphine may be distinguished from such substances. For the detection of morphine in highly diluted solutions, the author of this method advises to moisten slips of unsized paper repeatedly with the alkaloidal solution, carefully drying them between each immersion, and then apply the iodic acid solution and ammonia to the paper thus prepared.

Another method for detecting the eliminated iodine is by means of *carbon disulphide*, which will dissolve it with a more or less marked color. For this purpose, a few drops of a strong solution of iodic acid are agitated in a small test-tube with an equal volume of carbon disulphide, and then, if no coloration is produced, a small portion of the alkaloid or of its saline solution is added and the mixture again agitated, when, on repose, the disulphide liquid will subside and present a color varying from a faint light pink to deep dark red, depending upon the quantity of morphine present.

In this manner, 1–100th grain of morphine will yield a deep pink coloration, which is quickly discharged by a drop of ammonia. One drop of a 1–5000th solution of the alkaloid will cause a distinctly marked pinkish hue. This method is open to the same fallacies as the starch reaction.

5. *Ferric Chloride.*

Concentrated solutions of salts of morphine, as well as the alkaloid or any of its salts in the solid state, strike with a *neutral* solution of ferric chloride, or of ferric sulphate, providing no free acid is present, a deep blue color, which is discharged by free acids, by the caustic alkalies, and by heat. On the addition of nitric acid the blue mixture acquires an orange-red color.

1. $\frac{1}{100}$ grain of morphine, in solution in one grain of water, yields with a drop of the reagent a quite good, ink-blue coloration.
2. $\frac{1}{500}$ grain: after a few minutes the reaction is evident, but not satisfactory.

The reaction of this reagent is much more delicate when applied to morphine in its solid state. Thus, if a drop of the reagent be flowed over a 1–1000th grain residue of the alkaloid, it will yield

a deep blue color; and even with the 1–10,000th of a grain the reaction is still quite marked.

Ferric chloride also occasions with tannic and gallic acids a blue color, which is changed to reddish-yellow by nitric acid. When either of these vegetable acids is treated with nitric acid alone, it yields a *yellow* solution; in this respect they differ from morphine. There are also some few vegetable infusions which, when treated with a ferric salt, give rise to a more or less blue coloration. On the other hand, it should be borne in mind that the blue color produced by morphine may not make its appearance if the alkaloid be mixed with certain foreign substances.

If a few drops of a solution of morphine be treated with a drop or two of a neutral solution of ferric chloride, and then a drop of a dilute solution of potassium ferricyanide be added, the latter salt is reduced by the alkaloid to potassium ferrocyanide, which, reacting on the ferric salt, produces *Prussian blue*, which imparts a deep blue color to the mixture. In this manner a 1–1000th solution of morphine will yield an intense deep blue mixture; a 1–10,000th solution, a clear blue color; and a 1–50,000th solution, a strongly marked green coloration.

According to M. Kieffer, who first advised this test, the reaction is not interfered with by heat, nor by free acids in moderate quantity; but excess of an alkali prevents it by acting upon the ferric salt. Neither is the test interfered with by the presence of gum, sugar, alcohol, glycerine, quinine, or atropine. We find, however, that the same reaction is produced by brucine, and by narcotine, and also by sulphites and similar reducing agents; but not by strychnine, papaverine, or meconin.

6. *Sulpho-Molybdic Acid.*

When morphine in its solid state, or any of its salts, is touched with a drop of sulphuric acid containing a little molybdic acid, it immediately dissolves, with the production of a beautiful purple or crimson color, which quickly passes through several shades, and after a time the mixture acquires a deep blue color, which generally appears first along the margin of the liquid and is more or less permanent. Sometimes the final color is green or brownish-green, or it may be yellow. This reaction was first observed by M. Froehde, in 1866.

The reagent may be prepared by dissolving three parts of molybdic acid, or of an alkali molybdate, in 100 parts of pure sulphuric

acid, by the aid of a moderate heat. Froehde advised to dissolve five milligrammes of the molybdic compound in one cubic centimetre of sulphuric acid (one part in 368 of acid). The reagent should be freshly prepared when required for use.

The exact nature of the reaction of this test is yet not fully understood. It is known, however, that in the final result a portion at least of the molybdic acid is reduced, a lower oxide of the metal being formed. The final blue color is discharged by hydrochloric acid and by free chlorine; also by nitric acid, which, when the morphine is present in not too minute quantity, changes it to a reddish or orange-red hue.

1. $\frac{1}{100}$ grain of morphine, as sulphate, in the dry state, when treated with a moderate drop of the reagent, yields an immediate, intense purple coloration. After one or two minutes the drop acquires a deep blue color along the margin, and soon the whole liquid assumes a deep blue color, which is permanent for at least some days.
2. $\frac{1}{1000}$ grain, with a minute drop of the reagent, yields much the same results as 1. If the mixture be stirred, the blue color may quickly disappear.
3. $\frac{1}{10,000}$ grain: a fine purple coloration, which after a little time disappears, and the liquid acquires a yellow hue. If the morphine residue be only *moistened* with the reagent, the purple color is soon changed into blue, which remains unchanged for half an hour or longer.
4. $\frac{1}{50,000}$ grain: if a minute drop of the reagent be flowed over the deposit, a very marked purple coloration manifests itself along the lines of the deposit; after a little time this color disappears, the liquid becoming colorless.
5. $\frac{1}{100,000}$ grain, treated as in 4, yields a distinct purple coloration, which quickly disappears.

The reaction of this test, like that of the color-test for strychnine, with which it is very analogous, will reveal itself with about the least quantity of morphine visible to the naked eye, and, when the test is performed under the microscope, with about the least crystal visible under a low power of the instrument. The reaction is produced by morphine and its ordinary salts, but when present in only very minute quantity the reaction of the free alkaloid and its sulphate is more satisfactory than that of the acetate and hydrochloride.

Fallacies.—Sulpho-molybdic acid produces a similar violet or purple coloration with *papaverine*, *salicin*, and *populin*. These substances, however, differ from morphine in that when treated with sulphuric acid *alone*, papaverine dissolves with a purple or violet color, and salicin and populin strike a red coloration; whereas morphine, when pure, dissolves without color.

Various alkaloids and similar principles will yield under the action of this reagent, either immediately or after a time, a more or less blue, green, brown, or yellow coloration; and even ordinary organic matter may after a time cause a blue color. These results, however, could not be confounded with the morphine reaction. Strychnine yields no coloration with the reagent.

7. *Potassium Iodide.*

This reagent produces in somewhat concentrated neutral solutions of salts of morphine, especially if the mixture be stirred or allowed to stand some time, a white, crystalline precipitate, which is readily soluble in acids, even acetic acid. This reaction is readily interfered with by the presence of foreign substances.

1. $\frac{1}{100}$ grain of morphine, in one grain of water, yields after a little time a quite copious deposit of large groups of crystalline needles, Plate VII., fig. 1. The precipitate from a solution of the sulphate of morphine is more prompt in forming, and somewhat more abundant, than that obtained from the acetate.
2. $\frac{1}{500}$ grain yields after some minutes a very good, granular deposit.

This reagent also produces white crystalline precipitates with several of the alkaloids, but the forms of these in most instances differ widely from those obtained from morphine.

8. *Potassium Chromate.*

Potassium chromate throws down from strong neutral solutions of salts of morphine a yellow, crystalline precipitate, which is very readily soluble in free acids.

1. $\frac{1}{100}$ grain of morphine yields in a very little time, especially if the mixture be stirred, a very copious, crystalline deposit, having the forms illustrated in Plate VII., fig. 2.
2. $\frac{1}{1000}$ grain yields after some time a slight granular precipitate.

Potassium dichromate produces in one drop of a 1–100th solution of the alkaloid a yellow, amorphous precipitate, which after a time

becomes granular. In solutions but little more dilute than this the reagent fails to produce a precipitate.

9. *Auric Chloride.*

Solutions of salts of morphine yield, with trichloride of gold, a bright yellow, amorphous precipitate, which almost immediately begins to darken, becoming bluish and finally dirty green or nearly black. Solutions of the sulphate of morphine do not seem to undergo this change as rapidly as those of the acetate. The precipitate is partially soluble in acetic and nitric acids. If the precipitate, as first produced, be treated with a solution of potassium hydrate, it immediately darkens, and the mixture becomes bluish, purplish, or nearly black, its exact color depending upon the relative quantity of reagent employed.

1. $\frac{1}{100}$ grain of morphine, in one grain of water, yields a very copious, yellow deposit, which undergoes the changes above described.
2. $\frac{1}{1000}$ grain yields after a few moments a very good, yellow precipitate, which slowly darkens. When treated with a drop of potassium hydrate solution, the precipitate dissolves, and the mixture, in a very little time, becomes purplish or nearly black.
3. $\frac{1}{10,000}$ grain: after a little time a good precipitate, which is readily soluble, to a clear solution, in potassium hydrate. After some minutes, however, the alkaline mixture deposits small black flakes.
4. $\frac{1}{25,000}$ grain yields, after standing some time, a quite distinct turbidity.

If the precipitate from ten or fifteen grains of a 1–1000th or stronger solution of the alkaloid be boiled in the mixture, the deposit, without dissolving, assumes a brown or dark color, due to its partial decomposition; the deposit from a 1–2500th solution readily dissolves upon heating, and the mixture on cooling immediately darkens, from the presence of small black flakes, which after a time adhere to the sides of the tube; the precipitate from a 1–5000th solution readily dissolves by heat, yielding a yellow solution, which undergoes but little change, even after several hours.

Besides morphine, tannic and gallic acids and certain other organic substances have the property of precipitating and reducing solutions of salts of gold. With the aid of potassium hydrate most organic

compounds precipitate the metal in the form of a black powder; and even a mixture of chloride of gold and potassium hydrate alone may after a time yield black flakes.

10. *Platinic Chloride.*

This reagent throws down from concentrated neutral solutions of acetate of morphine a yellow, granular precipitate, which is very readily soluble in acids, even acetic acid.

One grain of a 1–100th solution of the alkaloid yields, especially if the mixture be allowed to stand some time, a quite good, yellow deposit, Plate VII., fig. 3. Solutions but little more dilute than this fail to yield a precipitate.

11. *Iodine in Potassium Iodide.*

A solution of iodine in potassium iodide produces in solutions of salts of morphine, even when highly diluted, a reddish-brown amorphous precipitate, which is but slowly soluble in acetic acid, but dissolves readily to a clear solution in potassium hydrate; it is also soluble in alcohol. Unless large excess of the reagent be added, the precipitate after a time partially or entirely disappears. The reagent may be prepared by dissolving two parts of iodine and five parts of potassium iodide in 100 parts of water.

1. $\frac{1}{100}$ grain of morphine, in one grain of water, yields a very copious deposit.

After a few minutes the precipitate assumes a lighter color, becomes granular, and soon twig-like groups of crystals or plates appear, having various colors, being either orange-red, brown, yellow, or nearly black, Plate XIV., fig. 1. The formation of the crystals is much facilitated by stirring the mixture; and they are more readily obtained from the acetate and hydrochloride of morphine than from the sulphate. The presence of a trace of free acetic acid also promotes their formation.

2. $\frac{1}{1000}$ grain: a very good reddish-brown precipitate. After a time, especially if the mixture be stirred, beautiful groups of reddish-brown crystals may appear.
3. $\frac{1}{10,000}$ grain: an immediate turbidity, and in a little time a very fair, brownish-yellow deposit, which may become more or less crystalline.
4. $\frac{1}{60,000}$ grain yields a very satisfactory turbidity.

The production of a precipitate by this reagent is common to a large class of organic substances; yet the character of the crystals, when obtained, is rather peculiar to morphine. Codeine yields with the reagent somewhat similar crystals. The formation of the morphine crystals is readily prevented by the presence of foreign matter.

12. *Bromine in Bromohydric Acid.*

Neutral solutions of salts of morphine, when treated with a solution of bromohydric acid saturated with bromine, yield a yellow, amorphous precipitate, which after a time dissolves, but is reproduced upon further addition of the reagent. The precipitate is soluble in acetic acid and in alcohol.

1. $\frac{1}{100}$ grain of morphine yields a very copious precipitate, which remains amorphous.
2. $\frac{1}{1000}$ grain: a quite good deposit.
3. $\frac{1}{2500}$ grain yields a slight turbidity.

This reagent also produces similar precipitates with various other organic substances.

13. *Picric Acid.*

An alcoholic solution of picric acid produces in aqueous solutions of salts of morphine a bright yellow, amorphous precipitate, which is readily soluble in alcohol, but only slowly soluble in acetic acid. The precipitate remains amorphous.

1. $\frac{1}{100}$ grain of morphine, in one grain of water, yields a very copious deposit.
2. $\frac{1}{500}$ grain yields a quite distinct precipitate.
3. $\frac{1}{1000}$ grain: no indication.

This reaction is common to a great number of organic substances, but with several of the other alkaloids the reagent produces crystalline precipitates.

14. *Chlorine and Ammonia.*

When a strong solution of a salt of morphine is treated with a slow stream of chlorine gas, it acquires a deep yellow color, which, upon the addition of ammonia, is changed to deep brown. This color is not affected by large excess of ammonia or by acetic acid.

1. 1–100th solution of morphine: ten grains of this solution yield results similar to those just described.

2. 1–1000th solution: chlorine imparts to the liquid a yellow tint, which is changed to a quite distinct brownish hue by ammonia.

Solutions but little more dilute than the last-named show no change when treated with these reagents.

Other Reagents.—Potassium iodohydrargyrate, or a solution of corrosive sublimate containing just sufficient potassium iodide to redissolve the precipitate first produced, produces in solutions of salts of morphine, even when highly diluted, a dirty-white, gelatinous or flocculent precipitate of the double iodide of morphine and mercury, which is only very sparingly soluble in diluted acetic and hydrochloric acids, but readily soluble in large excess of alcohol.

The precipitate thus produced, especially when from somewhat dilute solutions of morphine, after a little time becomes in part or wholly converted into groups or bundles of fine, delicate, crystalline needles. In this manner the 1–1000th grain of morphine will yield a very good crystalline deposit, Plate XIV., fig. 2. A drop of a 1–10,000th solution of the alkaloid yields no immediate precipitate with the reagent, but after a time very long slender needles appear.

The production of a white or dirty-white precipitate by this reagent is common to a large number of organic principles; and in some instances, as in the present, the precipitate becomes more or less crystalline.

Tannic acid throws down from somewhat strong, neutral solutions of salts of the alkaloid a white, flocculent precipitate, which is readily soluble in acids and in the fixed caustic alkalies. *Palladium chloride* produces in similar solutions a yellow, amorphous precipitate, which is also readily soluble in acids.

When a few drops of a strong solution of a salt of morphine are treated with a strong solution of *silver nitrate,* the latter salt, especially if the mixture be gently heated, is sooner or later decomposed, with the production of a shining, crystalline precipitate of metallic silver; at the same time, the mixture acquires a more or less yellow hue, due to the action of the eliminated nitric acid upon the alkaloid. (J. Horsley, *Chem. News,* July, 1862, 6.) One grain of a 1–100th solution of morphine, when treated after this method, yields a very satisfactory deposit.

As a test for morphine, A. Jorissen has advised to heat the alkaloid with a few drops of pure sulphuric acid on a water-bath, then

add a minute crystal of *ferrous sulphate*, stir the crushed crystal in the liquid, and continue the heat for about a minute. The solution is then poured into a porcelain capsule containing a little strong ammonia, when the morphine solution will assume a red color, passing into violet at the margin, whilst the ammoniacal stratum will acquire a deep blue color. (*Chem. News*, Feb. 1882, 57.) 1–100th grain of morphine will, in this manner, produce a marked coloration. Codeine fails to respond to this reaction.

When a little morphine is treated with a drop of concentrated sulphuric acid holding in solution *titanic acid*, a red-brown color, passing to violet, is produced.

Potassium sulphocyanide, ferrocyanide, and ferricyanide, also lead acetate and barium chloride, fail to produce a precipitate, even in concentrated solutions of salts of morphine, at least so far as the alkaloid itself is concerned.

Among the tests now described for the detection of morphine, the reaction of no one of them, taken alone, as already intimated, is peculiar to the alkaloid. But by the concurrent action of two or more of them, especially the sulpho-molybdic acid, nitric acid, and ferric chloride tests, the true nature of even exceedingly minute quantities of the alkaloid may be fully established, especially if it be in the crystalline state. It may here be remarked that of the ordinary alkaloids morphine is one of the most difficult to recover, especially in its pure state, from complex organic mixtures.

III. Meconic Acid.

History.—Meconic acid was discovered, in 1804, by Sertürner. In its pure state it crystallizes in the form of colorless plates, either singly or in groups; its composition in this form is $H_3C_7HO_7,3H_2O$. In nature it has been found only in the poppy tribe, in which it exists as meconate of morphine. Of good Smyrna opium it forms about six per cent.; its proportion, however, varies in different samples of the drug, and it is even said to be sometimes altogether absent; but this statement is exceedingly doubtful.

Preparation.—Various methods have been proposed for the preparation of meconic acid, but we have found the following to be one of the most simple, at least if only a small quantity of the substance

be desired. A strong filtered aqueous solution of opium is treated with excess of lead acetate, and the impure *meconate of lead* thus produced collected on a filter and washed, as long as the washings become colored. It is then diffused in a small quantity of water and treated with excess of sulphuretted hydrogen gas, whereby the lead is precipitated as sulphide, while the liberated meconic acid enters into solution. The liquid is now filtered and evaporated on a water-bath at a very moderate heat, until a drop of it removed to a watch-glass, cooled, and stirred with a drop of hydrochloric acid, yields a crystalline precipitate. The liquid is then allowed to cool, and strongly acidulated with pure hydrochloric acid, when after a time the meconic acid, being insoluble in diluted hydrochloric acid, will separate in the form of shining plates and crystalline groups. Should the crystals not be entirely colorless, they may be redissolved in a small quantity of hot water, and the cooled solution again strongly acidulated with hydrochloric acid.

Physiological Effects.—Meconic acid, when taken into the system, seems to be inert. At least, it has repeatedly been administered to inferior animals in doses of several grains, and taken by man in similar quantities, without producing any appreciable effect.

General Chemical Nature.—As usually found in the shops, meconic acid is in the form of crystalline scales, having a more or less reddish color, due to the presence of foreign matter. It has an acid, astringent taste, and strongly acid properties, readily uniting with the metals, forming salts called *meconates*. It, like phosphoric and arsenic acids, is tribasic, or capable of uniting with three atoms of a monatomic metal. When the crystallized acid is heated, it first parts with its three molecules of water of crystallization, then fuses, emits dense, white fumes, and finally takes fire, burning with a yellow flame. If the acid be moderately heated in a reduction-tube, it sometimes yields a sublimate of crystalline needles.

Solubility.—Meconic acid is soluble in about one hundred and fifteen times its weight of pure *water*, at a temperature of 15.5° C. (60° F.), forming a strongly acid solution. It is much more freely soluble in hot water, from which, however, much of the excess separates, in the crystalline form, as the solution cools. In water containing free hydrochloric acid, meconic acid is very much less soluble than in pure water. *Alcohol* dissolves it rather freely, and leaves it, on spontaneous evaporation of the liquid, in the form of beautiful

groups of crystals. It is only very sparingly soluble in absolute *ether*, requiring about 2150 parts by weight of this liquid for solution; and it is almost wholly insoluble in *chloroform*. The *salts* of this acid, except those of the alkalies, which are freely soluble, are, for the most part, insoluble in water. They are also insoluble, or very nearly so, in alcohol.

SPECIAL CHEMICAL PROPERTIES.—Meconic acid, in its solid state, is unchanged in color by cold sulphuric, nitric, and hydrochloric acids. On the application of a very gentle heat, it dissolves quietly to a clear solution in the first two of these mineral acids, but it is insoluble in hydrochloric acid; at a little higher temperature it is readily decomposed by the mineral acids with effervescence. When heated to a temperature of 150° C. (302° F.), solid meconic acid, parting with its water of crystallization, is resolved into carbonic acid gas and a new dibasic acid, named *comenic;* thus: $H_3C_7HO_7 = H_2C_6H_2O_5 + CO_2$. At a somewhat higher temperature, comenic acid in its turn is resolved into carbonic acid gas and *pyromeconic* acid, which is monobasic: $H_2C_6H_2O_5 = HC_5H_3O_3 + CO_2$. Both these new acids, like the meconic, strike a deep blood-red color with solutions of ferric salts. The conversion of meconic into comenic acid is also effected by boiling an aqueous solution of the acid, the change being much facilitated by the presence of a free mineral acid. When boiled with an aqueous solution of either of the fixed caustic alkalies, meconic acid is resolved into carbonic and oxalic acids and a dark coloring matter.

In the following examination of the tests for meconic acid when in solution, pure aqueous solutions of the free acid were employed, it being dissolved, when necessary, by the aid of a very gentle heat. The fractions indicate the amount of crystallized acid present in one grain of the fluid. Unless otherwise indicated, the results refer to the behavior of one grain of the solution.

1. *Ferric Chloride.*

Solutions of ferric chloride and of ferric sulphate strike with solutions of meconic acid, as well as with the acid and its salts in the solid state, a deep blood-red color, which is not discharged by either corrosive sublimate or chloride of gold, but readily disappears upon the addition of a solution of stannous chloride. The red colora-

tion manifests itself in the presence of even large excess of either of the free mineral acids.

1. $\frac{1}{100}$ grain of meconic acid, in one grain of water, yields with a drop of the reagent a deep reddish-brown coloration, which requires several drops of either of the concentrated mineral acids for its discharge, but it is unaffected, further than by dilution, by several drops of a strong solution of either corrosive sublimate or chloride of gold.
2. $\frac{1}{1000}$ grain yields a very good red coloration.
3. $\frac{1}{10,000}$ grain: the mixture acquires a very distinct purplish-red color.
4. $\frac{1}{20,000}$ grain yields a just perceptible red tint. In several drops of this solution, the red coloration is quite distinct.

If the meconic acid solution be evaporated by a very gentle heat to dryness, and a drop of the reagent applied to the residue:

1. $\frac{1}{10,000}$ grain: the deposit assumes a deep blood-red color.
2. $\frac{1}{50,000}$ grain yields a very distinct red coloration.
3. $\frac{1}{75,000}$ grain: the residue acquires a just perceptible red hue.

This is the most characteristic test yet known for the identification of very minute quantities of meconic acid, yet it is open to some few fallacies; but these may be readily guarded against. They are as follows:

a. The *alkali sulphocyanides* and free *sulphocyanic acid* yield with ferric salts a red coloration not to be distinguished in appearance from that occasioned by meconic acid. This color, however, unlike that from meconic acid, is quickly discharged by a solution of corrosive sublimate. This latter reagent, therefore, serves to distinguish readily between these substances. It is frequently stated that the red color produced by a sulphocyanide is readily discharged by a solution of chloride of gold; but this is not the case.

Another method of distinguishing between the red colors produced by these different substances, as first proposed by Dr. Percy, is to place in the colored mixture a piece of pure zinc, and then add a drop of sulphuric acid, when in the case of meconic acid the color is slowly discharged with the evolution of pure hydrogen gas; whereas the color of a sulphocyanide is destroyed with the evolution of sulphuretted hydrogen gas, which may be recognized by its peculiar odor, and by its blackening a piece of paper moistened with a solution of lead acetate and suspended over the mixture. This

method is not as simple as the preceding; moreover, if the zinc should contain sulphur, as is frequently the case, the mixture will evolve sulphuretted hydrogen, even in the absence of a sulphocyanide.

Human saliva has not unfrequently the property of striking a red color with ferric salts, due to the presence of a sulphocyanide; and Dr. Pereira states (*Mat. Med.*, ii. 1033) that he has on several occasions obtained the same results from the liquid contents of the stomach of subjects in the dissecting-room. However, in the preparation of the contents of this organ for the detection of meconic acid, as pointed out hereafter, any sulphocyanide present would be separated with the foreign matter, when this objection would no longer hold. If in any case there is any doubt as to the true nature of the red coloration, this, of course, may be removed by the application of a solution of corrosive sublimate.

b. Strong solutions of *acetic acid* and of its neutral salts yield with the iron reagent a more or less red coloration, which, like that from meconic acid, is unaffected by corrosive sublimate and chloride of gold. This color is more readily affected by free mineral acids than that from the opium compound. Solutions of acetic acid and of its salts differ from those of meconic acid, in that they fail to yield a precipitate with lead acetate.

c. Ferric salts also strike with a concentrated decoction of *white mustard*, due to the presence of sulphocyanide of sinapine, a red color, which, however, is immediately discharged by corrosive sublimate, but not by chloride of gold.

Besides the substances now mentioned, a strong infusion of *Iceland moss*, and of some few other rare substances, as first pointed out by Dr. Pereira, will also yield a more or less red coloration with the iron reagent; but these substances are uncrystallizable, and, like those before mentioned, would be removed from the liquid during its preparation for the application of the test for meconic acid. The color produced from Iceland moss has a purplish hue, and is unaffected by corrosive sublimate, but it is immediately destroyed by chloride of gold.

2. *Lead Acetate.*

This reagent throws down from solutions of free meconic acid and of its soluble salts a yellowish or yellowish-white, amorphous precipitate of meconate of lead, $Pb_3 2C_7HO_7, Aq$, which is insoluble

in large excess of acetic acid, but readily soluble, to a clear solution, in diluted nitric acid. If the precipitate be treated with a drop of ferric chloride solution, the mixture acquires a red color.

1. $\frac{1}{100}$ grain of meconic acid, in one grain of water, yields a very copious, yellowish deposit.
2. $\frac{1}{1000}$ grain: a copious, yellowish-white precipitate.
3. $\frac{1}{10,000}$ grain yields a very distinct deposit.
4. $\frac{1}{50,000}$ grain: after a few minutes a quite distinct opalescence appears, and then little whitish flakes.

Acetate of lead also produces precipitates with many other substances, but in these cases the deposit has always, unless foreign matter be present, a pure *white* color. Among these substances may be mentioned:

a. Sulphocyanides, which yield a white precipitate which, like that from meconic acid, is reddened by ferric salts; but it is readily *soluble* in *acetic acid*, and when from strong solutions, insoluble in diluted nitric acid; when from dilute solutions, however, it is readily soluble in the latter acid to a clear solution. When treated with metallic zinc and sulphuric acid, sulphocyanide of lead undergoes decomposition with the evolution of sulphuretted hydrogen; whereas the meconate of lead, as already stated, yields pure hydrogen gas. *b. Chlorine* yields with the reagent a white precipitate, which when from sodium chloride is readily soluble in excess of the precipitant, and in acetic and nitric acids; but when due to free chlorine, it is only sparingly soluble in these acids. *c. Sulphuric* acid, either free or combined, yields a precipitate which is insoluble in acetic acid, and only sparingly soluble in nitric acid. *d.* Soluble *carbonates* occasion a precipitate that is readily soluble with effervescence in acetic acid. *e. Phosphates* and *oxalates*, also, yield precipitates which are insoluble in acetic acid, but readily soluble in nitric acid. So, also, the reagent produces white precipitates with various organic principles; but these deposits are readily distinguished from the meconic acid compound, in not being reddened by persalts of iron.

3. *Barium Chloride.*

Strong aqueous solutions of meconic acid and of its alkali salts yield with barium chloride a white crystalline precipitate of barium meconate, which is insoluble in acetic and diluted nitric acids, and also in caustic ammonia.

1. $\frac{1}{100}$ grain of meconic acid: in a few moments crystals begin to appear, and in a very little time there is a quite copious, crystalline deposit, of the peculiar forms illustrated in Plate VII., fig. 4. If on the addition of the reagent the mixture be stirred, it immediately yields a copious crystalline deposit.
2. $\frac{1}{500}$ grain: after a little time, especially if the mixture be stirred, there is a quite satisfactory deposit, consisting principally of little masses of aggregated granules.
3. $\frac{1}{1000}$ grain: after some time the mixture yields small, microscopic granules.

Although this reagent also produces white precipitates in solutions containing sulphuric, phosphoric, and several other acids, yet the crystalline form of the meconic acid deposit is peculiar.

4. *Hydrochloric Acid.*

This acid, in its free state, produces in aqueous solutions of meconic acid and of its soluble salts, when not too dilute, a white precipitate of free meconic acid, due to the insolubility of the latter in the presence of a limited quantity of the mineral acid. This precipitate is in the form of transparent crystalline plates, which, for the most part, are arranged in beautiful groups, and many of which, when examined by transmitted light under the microscope, appear beautifully colored. The formation of the precipitate is much facilitated by stirring the mixture with a glass rod.

1. $\frac{1}{100}$ grain of meconic acid, in one grain of water, when treated with a drop of concentrated hydrochloric acid: almost immediately crystals begin to form, and in a little time there is a quite copious deposit, Plate VII., fig. 5.
2. $\frac{1}{500}$ grain: after some minutes, providing very large excess of hydrochloric acid be not employed, the mixture throws down a very satisfactory, crystalline precipitate.

Hydrochloric acid also produces white precipitates in solutions containing silver, lead, antimony, and mercurous combinations. But the silver, mercury, and antimony deposits are amorphous, and that from lead is in the form of crystalline needles; whereas the meconic acid precipitate, even from complex organic mixtures, is always in the form of crystalline plates. It need hardly be remarked that the meconic acid precipitate also differs from these fallacious substances in striking a red color with persalts of iron.

5. *Silver Nitrate.*

This reagent produces in aqueous solutions of the organic acid an amorphous precipitate of silver meconate, which is readily soluble in ammonia and in nitric acid, but insoluble in acetic acid. The color of this precipitate depends somewhat upon the relative quantity of reagent employed: when the latter is in excess, the deposit has a yellow color; whilst if there is excess of meconic acid present, the precipitate is white. The yellow precipitate consists of the tribasic meconate of silver, $Ag_3C_7HO_7$; while the white is a dibasic salt of the metal, $Ag_2HC_7HO_7$.

1. $\frac{1}{100}$ grain of meconic acid, in one grain of water, yields a very copious, pale yellow or yellowish-white, gelatinous precipitate, which after a time acquires a pure yellow color. If several drops of the solution be precipitated by excess of the reagent, the deposit has at once a rather bright yellow hue.
2. $\frac{1}{1000}$ grain: a good, flocculent precipitate, having only a just perceptible yellow tint.
3. $\frac{1}{10.000}$ grain: after a time a quite distinct flaky deposit.

Silver nitrate also produces yellow or yellowish-white precipitates in solutions containing phosphoric, arsenious, and silicic acids; but neither of these acids strikes a red color with persalts of iron.

6. *Potassium Ferrocyanide.*

Strong aqueous solutions of meconic acid and of its alkali salts, when treated with this reagent, yield, especially if the mixture be stirred and allowed to stand, a crystalline precipitate, which is only slowly soluble in acetic acid.

One grain of a 1–100th solution of the free acid yields after a little time large groups of hair-like crystals, Plate VII., fig. 6; after about half an hour the mixture becomes converted into an almost solid crystalline mass. Solutions but little more dilute than this altogether fail to yield a precipitate. The crystals produced by this reagent are quite characteristic.

7. *Calcium Chloride.*

This reagent produces in concentrated solutions of the alkali meconates a white or yellowish-white precipitate of meconate of calcium. One grain of a 1–100th solution of the free acid yields no

immediate precipitate, but after a little time large groups of colorless transparent crystals separate from the mixture, Plate VIII., fig. 1. The precipitate is insoluble in large excess of acetic acid; its formation is much facilitated by agitating the mixture.

Other Reagents.—Copper sulphate solution throws down from strong aqueous solutions of meconic acid a greenish-blue, amorphous precipitate of meconate of copper, which is soluble in acetic acid and in ammonia. Ammonio-copper sulphate fails to produce a precipitate, even in concentrated solutions of the free acid.

Saturated aqueous solutions of the free acid fail to yield a precipitate with either of the following reagents: auric chloride, potassium ferrocyanide, picric acid, platinic chloride, corrosive sublimate, iodine in potassium iodide, bromine in bromohydric acid, tannic acid, and potassium chromate.

Separation of Meconic Acid and Morphine from Solutions of Opium and Complex Organic Mixtures.

The presence of *opium* may be established, as already stated, by showing the presence of meconic acid and morphine. In fact, this may be done by simply proving the presence of *meconic* acid; yet, when possible, it is always advisable to prove also the presence of morphine. Should there be a failure to detect either of these substances, it is pretty certain that there would also be a failure to discover any of the other principles peculiar to the drug. This arises from the fact that the methods at present known for the separation of these latter substances from complex organic mixtures are much less delicate than those for the recovery at least of meconic acid. In their pure state, however, some of these principles may be identified in even smaller quantity than the organic acid. Before proceeding to the preparation of a suspected mixture for the application of chemical tests, it should be carefully examined for the *odor* of opium; this, however, may not be recognized even when the drug is present in quite notable quantity.

Suspected Solutions and Contents of the Stomach.—If the liquid presented for examination appears to be a simple aqueous solution of opium or laudanum, as is sometimes the case, it is slightly acidulated with acetic acid, and evaporated at a low temperature, on

a water-bath, to a small volume, then filtered, and the filtrate examined in the manner hereafter directed. When, however, the suspected mixture is of a complex nature and contains organic solids, these are cut into very small pieces, the mass, if not already sufficiently liquid, treated with pure water and a little alcohol, and the whole distinctly acidulated with acetic acid. It is then very moderately heated, with frequent stirring, for half an hour or longer, allowed to cool, the liquid strained through muslin, and the solid residue on the strainer well washed with strong alcohol and strongly pressed, the washings being collected with the first liquid. The united liquids are now concentrated to a very small volume, on a water-bath at a temperature not exceeding 71° C. (160° F.), and then, after cooling and dilution with water if necessary, filtered through paper previously moistened with water. Any solid matter thus separated is washed with a little diluted alcohol, and the washings added to the first filtrate. If during the concentration of the liquid much solid matter separates, it should be removed by a muslin strainer.

The clear filtrate thus obtained is treated with slight excess of lead acetate, by which any meconic acid present will be precipitated as meconate of lead, together with more or less foreign matter; at the same time, any morphine and other opium principles present will remain in solution. Should the liquid contain a sulphocyanide, this will also remain in solution, since, as already pointed out, these salts are not precipitated in the presence of free acetic acid by the lead reagent. When the precipitate has completely subsided, the mixture is transferred in small portions to a small moistened filter, and the solid residue left on the filter washed with a little pure water, this being collected with the first filtrate. The analysis now divides itself into two branches:

1st. *Contents of the filter.*—While the filter is still moist, its lower end is pierced with a glass rod, and the contents carefully washed by a jet of water from a wash-bottle into a tall test-tube, and the precipitate allowed completely to subside. After, if thought best, decanting a portion of the clear supernatant liquid, the precipitate is diffused in the remaining fluid and treated with a stream of sulphuretted hydrogen gas, as long as a precipitate is produced. By this treatment any meconate of lead present will be decomposed, the metal being thrown down as black sulphide, while the liberated

meconic acid will enter into solution. The liquid is then filtered, and the filtrate concentrated at a moderate temperature on a water-bath, when the excess of sulphuretted hydrogen present will be dissipated. If the liquid contains a quite notable quantity of meconic acid, it will now usually have a more or less reddish or brownish color.

After the solution thus obtained has cooled, a drop of it is removed to a watch-glass and tested with a ferric salt; if this indicates the presence of meconic acid in quite notable quantity, the remaining liquid is examined by some of the other tests for the organic acid. Should, however, the iron-test fail to yield positive results or indicate the presence of the acid in only minute quantity, the remaining fluid is carefully concentrated to a very small volume, and consecutive drops examined by ferric chloride, hydrochloric acid, and barium chloride or potassium ferricyanide. Should, in any case, the iron-test fail, it is quite certain that the other tests mentioned would also fail, since the former is much the more delicate in its reactions. If the concentrated liquid contains much foreign matter, this may very much interfere with the normal reactions of the tests. Under these circumstances, the liquid may be evaporated at a very gentle temperature to dryness, the residue extracted with a small quantity of strong alcohol, the filtered alcoholic extract evaporated to dryness, and the residue thus obtained dissolved in a very small quantity of warm water and the solution then tested. In some instances, however, it will be found best, for the separation of foreign matter, to reprecipitate the meconic acid by lead acetate, and then treat the precipitate in the manner above described.

By the method now described, the 1–100th of a grain of meconic acid in solution in twenty-five grains of water may be precipitated and recovered without any appreciable loss. So, also, an alcoholic solution of *one grain of opium* mixed with foreign organic matter, when treated after this method and the final solution reduced to four drops, gave with the four reagents before named results somewhat better in each case than a 1–100th solution of the pure acid, the last three reagents producing copious crystalline precipitates of the forms peculiar to the organic acid.

When a solution has been prepared in this manner, the fallacies attending the iron-test under certain conditions do not apply. The manner in which any sulphocyanide present would be avoided has already been indicated; and, as the acetates are all soluble, they

also would remain in solution in the filtrate; nor could any of the organic infusions that strike a red color with the iron reagent remain on the filter with the washed meconate of lead.

Another method frequently advised for decomposing the meconate of lead for the recovery of the organic acid, is to digest it at a moderate heat with diluted sulphuric acid, under the action of which it is resolved into insoluble lead sulphate and free meconic acid, which enters into solution. Since, however, as already pointed out, meconic acid is prone to undergo decomposition in the presence of a free mineral acid, especially if the mixture be heated to near the boiling temperature, this method may be attended with considerable loss; moreover, the presence of sulphuric acid would interfere with some of the tests for the organic acid.

2d. *The filtrate.*—The above filtrate—which contains the morphine in the form of acetate, and some of the other opium principles, together with any excess of lead acetate employed in the precipitation of the meconic acid—is treated with excess of sulphuretted hydrogen gas, for the purpose of precipitating the lead. When the precipitate has completely deposited, which may be facilitated by the application of a very gentle heat, the liquid is filtered, and the filtrate evaporated on a water-bath to dryness; the residue thus obtained is well stirred with a little pure water, and the solution again filtered. A drop of the solution may now be tested for morphine by nitric acid, and another by ferric chloride. Whether these tests indicate the presence of the alkaloid or not, the remaining liquid, after dilution if necessary, is rendered slightly alkaline by a strong solution of sodium carbonate, allowed to stand some little time, and then agitated with a few volumes of *absolute ether*. This liquid will extract some of the opium principles and more or less coloring matter, but leave the liberated morphine in the alkaline aqueous fluid. After carefully decanting the ethereal liquid, and placing it aside for future examination if necessary, the alkaline liquid may be examined by either of the following methods.

a. Alcoholic-ether.—The liquid is violently agitated for some minutes with from four to five times its volume of a mixture consisting of two parts of *absolute ether* and one part of *pure alcohol*, by which the alkaloid will be extracted from the aqueous fluid. This operation is best performed by placing the alkaline liquid in a long graduated tube, and then adding sufficient of the prepared ethereal

mixture so that after agitation and repose the volume of the former liquid is slightly diminished. In certain proportions the liquids will form a homogeneous mixture, while in others the volume of the aqueous fluid will be augmented, and in others still it will be diminished. If any difficulty is experienced in regard to the separation of the liquids, a little pure ether should be added.

The *alcoholic-ether* is now carefully decanted into a watch-glass or capsule, and allowed to evaporate spontaneously, when the morphine will usually be left in its crystalline form; when, however, there is only a minute quantity of the alkaloid present or it is mixed with much foreign matter, it may remain in its amorphous state. When the residue has become quite dry, it is carefully washed, by gently rotating a few drops of pure water over it in the glass and then decanting the liquid. Small portions of the residue are now separately examined by nitric acid, sulpho-molybdic acid, and the iron-tests, and any remaining portion dissolved, by the aid of a trace of acetic acid, in a very small quantity of water, and the solution then submitted to some of the liquid tests for morphine. By exposing a portion of the aqueous solution to the vapor of ammonia until it acquires a very slightly alkaline reaction, and then exposing it to the air for several hours if necessary, the alkaloid may be deposited in its crystalline form, even when present in only very minute quantity. In this manner we have on several occasions obtained very satisfactory crystals, when every other method failed to reveal the alkaloid in this form.

On applying the method now described, for the extraction of morphine, to a complex organic mixture containing only *one grain of opium*, the meconic acid having been previously precipitated from the aqueous solution by lead acetate, the alcoholic-ether left on spontaneous evaporation a very fine crystalline deposit of the alkaloid.

b. Amyl alcohol.—Another method for the extraction of the morphine, is to agitate the alkaline liquid, as first suggested by Uslar and Erdmann (see *ante*, 424), with two or three times its volume of hot *amyl alcohol*, in which, as already shown, the alkaloid is rather freely soluble. When the fluids have completely separated, the upper, or alcoholic, liquid is transferred, by means of a caoutchouc pipette, to a watch-glass; the aqueous fluid is then washed with a fresh portion of the hot alcohol, and this transferred to the watch-glass containing the liquid first employed. In the absence of a

caoutchouc pipette, the alkaline liquid may be removed from the alcoholic by closing the upper end of an ordinary pipette with the finger and passing the open end to the bottom of the fluid mixture, when, upon removing the finger, the aqueous liquid will be forced into the tube, and may thus be removed. The employment of the ordinary suction-pipette, on account of the injurious action of the alcohol on the respiratory organs, is inadmissible.

The amyl alcohol is now evaporated, at a very gentle heat on a water-bath, to dryness, when the alkaloid may be left in its crystalline form; but it is much less apt to be left in this form, under these circumstances, than when separated by spontaneous evaporation from the above ethereal mixture. Should the residue be amorphous, it may be redissolved in a small quantity of diluted, ordinary alcohol, and the liquid allowed to evaporate spontaneously. The residue is then examined in the ordinary manner.

In the application of this method for the recovery of minute quantities of morphine from complex mixtures containing known quantities of opium, we have obtained very satisfactory results; and on the whole, perhaps, this process is preferable to the ether method before described.

c. Acetic ether.—A third method that may be employed for the extraction of the alkaloid from the foregoing alkaline solution, is by means of *acetic ether*, as advised by M. Alfred Valser. (*Chem. News*, 1864, ix. 289; from *Jour. de Pharm. et Chimie*, xliii. 49, 63.) The operation may be conducted in much the same manner as when amyl alcohol is employed, and the liquid allowed to evaporate spontaneously. If this method be adopted, it should be borne in mind that morphine is much less soluble in pure acetic ether than in either amyl alcohol or a mixture of alcohol and ether; and, therefore, that a correspondingly larger proportion of this liquid will be required for the extraction of a given quantity of the alkaloid. On the other hand, this liquid, when pure, has a much less solvent action upon foreign organic matter than either of the other liquids named, particularly a mixture of alcohol and ether; at the same time it is more likely than amyl alcohol, on evaporation, to leave the alkaloid in the crystalline form. It may here be remarked that acetic ether, as found in the shops, not unfrequently contains so much alcohol as to cause it to mix in all proportions with water, when agitated with this liquid.

The *absolute ether* with which the alkaline solution was washed, previous to the extraction of the morphine, contains narcotine and some other opium principles, together with more or less foreign organic matter. When evaporated spontaneously, it usually leaves, if there is not much foreign matter present, a transparent amorphous residue, which when treated with a drop of concentrated sulphuric acid dissolves to a blood-red solution; if a small crystal of potassium nitrate be stirred in this mixture, the color of the latter is changed to brownish or purplish. These results, however, being due to the combined action of several different substances, are subject to considerable variation.

Porphyroxin.—For the detection of small quantities of opium, Merck advises to take advantage of the property possessed by porphyroxin, one of the constituents of the drug, of being reddened when heated with hydrochloric acid. For this purpose the opium solution is rendered alkaline by potassium hydrate, and agitated with pure ether, in which this principle is soluble. A strip of white bibulous paper is then repeatedly dipped into the decanted ethereal liquid, the paper being dried between each immersion; the paper is now moistened with hydrochloric acid, and exposed to the vapor of boiling water, when it will acquire, especially after drying, a more or less rose-red color. On following these directions for the examination of solutions containing very notable quantities of opium, we failed to obtain very satisfactory results; with larger quantities of the drug, however, the red coloration was well marked.

According to Merck, *porphyroxin*, in its pure state, may be obtained by the following process. Powdered opium is exhausted by boiling ether, then made into a pulp with water, slight excess of potassium carbonate added, the mixture agitated with ether, the ethereal liquid evaporated to dryness, the residue thus obtained dissolved in a small quantity of very dilute hydrochloric acid, and the solution rendered slightly alkaline by ammonia, by which the porphyroxin, together with paramorphine, will be precipitated. On dissolving the precipitate in ether, and allowing the liquid to evaporate spontaneously, the former of these principles is left in the form of a resin, while the latter is deposited in the crystalline form. They may now be separated by cautiously treating the mixture with alcohol, in which the porphyroxin is soluble; the alcoholic solution is then evaporated to dryness at a low temperature. Porphyroxin

is described as a neutral substance, which crystallizes in brilliant needles, is readily soluble in alcohol and in ether, but insoluble in water. It is but proper to add that the existence of this substance, as a distinct opium principle, has been doubted by several experimentalists. According to O. Hesse, it consists of a mixture of several distinct principles.

Examination for Morphine alone.—When there is reason to suspect that morphine, or one or other of its salts, is present in its free state, the same method of analysis may be followed as for its recovery from organic solutions containing opium, except that the use of lead acetate is omitted. Thus, the mixture, slightly acidulated with acetic acid, is digested at a moderate temperature with diluted alcohol, allowed to cool, the liquid strained, then concentrated on a water-bath to a small volume, filtered, and the filtrate evaporated to dryness. The residue, thus obtained, is treated with a small quantity of water, the solution filtered, the filtrate rendered slightly alkaline with sodium carbonate, washed with *absolute ether*, and the alkaloid, if present, extracted by either of the methods heretofore described.

It rarely happens, under these circumstances, that the analyst is able to determine the acid with which the morphine was combined. Should, however, the mixture be not too complex, it may be concentrated on a water-bath to a very small volume, then gently warmed with a little concentrated alcohol, and the filtered liquid allowed to evaporate spontaneously, when the morphine salt may be deposited in its crystalline state. A portion of any deposit of the salt thus obtained is dissolved in a small quantity of pure water, and the nature of the acid determined by appropriate tests.

From the Tissues.—Thus far, with few exceptions, there seems to have been an entire failure to recover the poison from the tissues, in poisoning by opium, and its active alkaloid. And in the examination of the liver of two different animals poisoned by the drug, we met with similar results. If it be desired to examine the tissues for the absorbed poison, the solid organ, as a portion of the liver, cut into very small pieces and triturated in a mortar, is made into a thin paste with water containing a little alcohol, then acidulated with acetic or sulphuric acid, and the whole digested, with frequent stirring, at a moderate heat for about an hour. When the mass has cooled, the liquid is strained through muslin, and the solids upon the strainer well washed with diluted alcohol and strongly pressed.

The mixed liquids may then be examined after the manner already described.

From the Blood.—Among various methods pursued for the recovery of minute quantities of meconic acid and morphine, when purposely added to healthy blood, the following gave the best results. The fluid, acidulated with acetic acid in the proportion of about eight drops of the concentrated acid for each fluid-ounce of blood, is thoroughly agitated, best in a tolerably wide-mouthed bottle, with an equal volume of strong alcohol, and the mixture gently heated in a porcelain dish on a water-bath, until the albuminous matter has collected into little flakes. The cooled mass is thrown on a wet linen strainer, and the solids well washed with alcohol and strongly pressed. These are again thoroughly mixed with fresh alcohol, gently warmed, and the liquid strained as before. The united strained liquids are now concentrated on a water-bath to a small volume, again strained, and then filtered. If during the concentration of the liquid much solid matter separates, as is usually the case, it is removed by a strainer.

The filtered liquid thus obtained is evaporated to dryness on a water-bath, the residue digested with a small quantity of nearly absolute alcohol, the solution filtered, and the filtrate evaporated to dryness. This residue is gently warmed with a small quantity of water, and the liquid filtered. On now treating the filtrate with lead acetate, any meconic acid present will be precipitated as meconate of lead: it should be borne in mind that under these circumstances the lead reagent not unfrequently produces a yellowish-white precipitate, even in the absence of meconic acid. Any precipitate thus obtained is separated by a filter and examined in the usual manner for the organic acid, while the filtrate is tested for morphine.

The repeated digestions with alcohol, in the above process, are rendered necessary on account of the extreme tenacity with which these opium principles, especially the meconic acid, adhere to the albuminous matter of the blood. In fact, this organic acid forms with albumen a precipitate, which is very sparingly soluble in water, and only slowly yields the acid to alcohol.

In operating on a fluid-ounce of blood, according to this method, the smallest quantities of meconic acid and morphine from which we succeeded in recovering crystals of both substances were the *one-twentieth* of a grain of each. In one of these instances, the final morphine solution being concentrated to three drops, two of the drops

gave respectively with nitric acid and ferric chloride very satisfactory evidence of the presence of the alkaloid, while the third, when exposed to the vapor of ammonia, and then to the air for several hours, deposited four comparatively large groups of crystals of the pure alkaloid. In the same case, the evidence of the presence of the meconic acid was about equally satisfactory.

With mixtures containing smaller quantities of the opium principles, the final solutions, even when only the 1–100th of a grain of each substance had been added, gave results that no doubt were due to the presence of these principles; yet the reactions were by no means conclusive. On examining for only one of these substances, crystals may be obtained from a somewhat smaller quantity of either than before stated.

On applying the foregoing method to the examination of the blood of eight different dogs and cats poisoned by opium, the final solutions in some instances gave results which there is little doubt were due to the presence of meconic acid and morphine; while in others they failed to reveal the presence of a trace of either of these substances. In no instance, however, were crystals obtained or were the results, with perhaps a single exception, such as would have been satisfactory in an unknown case.

In the exception just mentioned, two grains of morphine in solution had been given to a large cat; an hour afterward an ounce of laudanum was administered, and in another hour one ounce more. In an hour after the last dose the animal was killed by a blow on the head, and four ounces of blood were carefully taken from the body. On treating the whole of the fluid after the manner before described, and concentrating the final solution, supposed to contain meconic acid, to two drops, and testing one of these directly with ferric chloride, and evaporating the other to dryness and testing the residue in the same manner, both gave results identical with those occasioned by minute traces of the organic acid. So, also, the morphine solution, when reduced to two drops and these tested separately by nitric acid and a ferric salt, gave equally distinct evidence of the presence of the alkaloid.

Bearing in mind that at most only a minute quantity of the organic poisons enters the blood, and the great loss attending the separation of the opium principles from this fluid, we were not much disappointed in the results of the foregoing experiments.

THE URINE.—According to M. Bouchardat, morphine, when taken either in its free state or under the form of opium, speedily appears in the urine, and may be detected by the liquid yielding a reddish-brown precipitate with a solution of iodine in potassium iodide. Since, however, as we have already seen, this reagent also produces similar precipitates with most of the other alkaloids and with certain other organic substances, this reaction in itself could by no means be regarded as direct proof of the presence of this alkaloid. Moreover, we find that the reagent not unfrequently throws down a precipitate from what may be regarded as normal urine; while, on the other hand, it sometimes fails to produce a precipitate, even when comparatively large quantities of the alkaloid have been purposely added to this liquid.

FAILURE TO DETECT THE POISON.—It has not unfrequently happened that there was a failure to detect a trace of either meconic acid or morphine in any part of the alimentary canal, even when large quantities of the poison had been taken and the conditions for its detection were apparently very favorable. Thus, in a case related by Dr. Christison, he failed to obtain any direct evidence of the presence of the poison in the contents of the stomach of a young woman who died in five hours after taking not less than two ounces of laudanum. In another case, the contents of the stomach, evacuated two hours after seven drachms of laudanum were swallowed, had no odor of opium, nor did they reveal the presence even of meconic acid.

Prof. L. A. Buchner relates an instance in which he failed to find any morphine in the stomach of a boy, five years old, who was killed by three doses, of two grains each, of the acetate of morphine. (*Amer. Jour. Pharm.*, Sept. 1867, 415.) And Dr. Ebertz reports a case (*Ann. d'Hyg.*, 1875, 220) in which a woman took in mistake for quinine about four grains (.25 gramme) of the hydrochloride, and died from its effects in from forty to fifty minutes. On examination of the contents of the stomach, the upper portion of the small intestines, the liver, spleen, kidneys, and the blood of the right ventricle, no trace of morphine was found. So, also, Dr. Ogston mentions a case (*Med. Jur.*, 1878, 567) in which a woman had taken not less than from nine to ten grains of the hydrochloride, and died within a few hours, and, although there had been no vomiting and no remedy applied, a most careful examination by himself and the late Prof.

Gregory failed to detect any trace of morphine in the alimentary tube or elsewhere.

Since the tests and methods for separating meconic acid from foreign substances are somewhat more satisfactory than those for morphine, in poisoning by opium, the acid has sometimes been detected when there was a failure to detect the alkaloid.

On the other hand, the poison has been detected even when taken in only comparatively small quantity and death was delayed for several hours. In a case related by Dr. Skae, in which not more than half an ounce of laudanum had been taken, and death did not occur until thirteen hours afterward, the contents of the stomach furnished evident indications of the presence of morphine, and faint evidence of meconic acid. It need hardly be remarked that, since opium or its active alkaloid is so frequently administered medicinally, the detection of mere traces of the poison in the dead body would not in itself be positive proof that it was the cause of death.

Quantitative Analysis.—For the purpose of estimating the quantity of morphine present in an aqueous solution of any of its salts, the somewhat concentrated solution may be slightly supersaturated with pure aqua ammoniæ, and allowed to stand quietly in a cool place for about twenty-four hours. The alkaloid, with the exception of the merest trace, will now be precipitated in its crystalline form. The crystals are then carefully separated from the liquid, washed with absolute ether, dried at the ordinary temperature, and weighed. One hundred parts by weight of the pure crystallized alkaloid represent 123.8 parts of crystallized hydrochloride of morphine, $C_{17}H_{19}NO_3,HCl,3Aq$; 125 parts of the crystallized sulphate, $2C_{17}H_{19}NO_3$; $H_2SO_4,5Aq$; or 131.6 parts of the acetate of morphine, $C_{17}H_{19}NO_3,C_2H_4O_2,3Aq$.

The quantity of opium or morphine found in the stomach, in poisoning by one or other of these substances, is usually too minute to admit of a direct quantitative analysis. Under these circumstances, the quantity may sometimes be estimated with considerable accuracy by observing the intensities of the reactions of the reagents applied, and comparing these with the reactions of known quantities of the poison.

IV. Narcotine.

History.—The existence of *narcotine* was first pointed out, in 1803, by Derosne; but Robiquet, in 1817, was the first to indicate its chemical nature. Blyth, in 1844, assigned to it the formula $C_{23}H_{23}NO_7$. The more recent investigations of Messrs. Matthiessen and Foster led them to adopt the formula $C_{22}H_{23}NO_7$. (*Jour. Chem. Soc.*, 1863, 342.) Wertheim has described three homologous forms of narcotine in opium, having the formulæ $C_{22}H_{23}NO_7$, $C_{23}H_{25}NO_7$, and $C_{24}H_{27}NO_7$, which he named, respectively, methylo-, ethylo-, and propylo-narcotine, from the fact that when passed over soda-lime they yield methylamine, ethylamine, and propylamine. The investigations of Matthiessen and Foster, as well as those of Dr. Anderson, however, render the existence of these varieties very doubtful.

Narcotine usually constitutes from six to eight per cent. of good Smyrna opium; but in some varieties of the drug it forms only about one per cent. As this substance may be extracted from the drug by ether, without the addition of either an alkali or an acid, it would appear that it exists principally in its free state. It has only feebly basic properties.

Preparation.—This substance may be obtained either by adding ammonia to the mother-liquor from which hydrochloride of morphine has been prepared, or by digesting the insoluble part of opium in acetic acid, and precipitating by ammonia. The impure narcotine is purified by digesting its hot alcoholic solution with animal charcoal and recrystallizing (Gregory).

Physiological Effects.—Much discrepancy has existed among experimentalists in regard to the action of narcotine upon the animal system, some observers considering it as almost inert, whilst others attribute to it narcotic properties. These narcotic effects, however, may have been due to the presence of morphine in the preparation employed. Dr. O'Shaughnessy, of Calcutta, attributed to it powerful antiperiodic properties, and used it, he states, with great success in the treatment of intermittent fever. He prescribed it in doses of three grains, three times a day.

Dr. S. Weir Mitchell, in experiments upon himself, found narcotine to produce little or no effect, even when taken in doses of thirty grains. It seemed to be equally inert when given by the mouth to

pigeons; but when administered hypodermically in two-grain doses, it caused feebleness, unsteady gait, and early convulsions, without in any instance stupor. (*Amer. Jour. Med. Sci.*, Jan. 1870, 23.) This observer also found that pigeons possessed an entire immunity to the action of opium and morphine, even when administered in enormous doses.

Chemical Properties.—In its pure state, *narcotine* crystallizes in the form of transparent, colorless, rhombic prisms; sometimes, however, it appears in the form of oblong plates, and at other times as a granular powder. In its solid state, it is nearly destitute of taste, but when in solution, it has an intensely bitter taste, even exceeding that of morphine. When moderately heated, it fuses to a colorless liquid; at higher temperatures it takes fire, burning with a smoky flame. According to Prof. Guy, narcotine fuses at 115.5° C. (240° F.), and volatilizes at 154.4° C. (310° F.).

Under the action of oxidizing agents narcotine is readily decomposed, giving rise to a variety of new compounds, among which is *opianyl*, one of the other opium principles. The pure alkaloid, when in solution, has little or no action upon reddened litmus-paper, in which respect it differs from morphine; so also, unlike morphine, it fails to strike a blue color either with a ferric salt or with a mixture of iodic acid and starch.

Narcotine fails to neutralize diluted acids, but it readily unites with them, forming salts, which, for the most part, are uncrystallizable. Concentrated *sulphuric acid* slowly dissolves the alkaloid to a yellow solution, which, when stirred with a crystal of potassium nitrate, acquires a deep blood-red color. When the simple acid solution is moderately heated, it acquires a purplish color, even when only a very minute quantity of the alkaloid is present. When the acid solution is stirred with a crystal of potassium dichromate, the results depend much upon the relative quantity of the salt employed (see *post*). Concentrated *nitric acid* also dissolves the alkaloid to a more or less yellow solution; *hydrochloric acid* dissolves it without change of color. It is slowly soluble in large excess of concentrated acetic acid, but insoluble in the diluted acid.

When large excess of powdered narcotine is digested for twenty-four hours, at the ordinary temperature, with pure *water*, this liquid fails to dissolve even the 1–20,000th of its weight of the alkaloid. Absolute *ether*, under similar circumstances, takes up one part of

the alkaloid in 208 parts of the liquid. Narcotine is soluble in all proportions in *chloroform*, and dissolves readily in *alcohol*, but is insoluble in the caustic alkalies. The salts of the alkaloid are, for the most part, readily soluble in water and in alcohol.

Narcotine and morphine may be separated from each other by agitating the mixture with chloroform or ether, which will dissolve the former but not the latter; so, also, these substances may be separated by a solution of either of the fixed caustic alkalies or by diluted acetic acid, which will take up the morphine but not the narcotine.

Narcotine may be readily separated from aqueous solutions of its salts by treating the solution with slight excess of a free alkali, and agitating the mixture with chloroform or ether. Upon spontaneous evaporation, the extracting liquid will usually leave the alkaloid in the form of beautiful groups of brilliant crystals, similar to those of the crystallized acetate (Plate VIII., fig. 3).

In the following examination of the reactions of narcotine when in solution, the pure alkaloid was dissolved in water by the aid of the least possible quantity of hydrochloric acid. The fractions employed indicate the amount of pure alkaloid in solution in one grain of water; and, unless otherwise intimated, the results refer to the behavior of one grain of the solution.

1. *The Alkalies and their Carbonates.*

The fixed caustic alkalies, and ammonia, as also their carbonates, produce in aqueous solutions of salts of narcotine a white precipitate of the free alkaloid, which is insoluble in even large excess of the precipitant and in diluted acetic acid, but readily soluble in hydrochloric and nitric acids. After a little time the precipitate becomes crystalline.

1. $\frac{1}{100}$ grain of narcotine, in one grain of water, yields a very copious, amorphous deposit, and very soon the mixture becomes a nearly solid crystalline mass.
2. $\frac{1}{1000}$ grain yields an immediate precipitate, which in a little time becomes converted into beautiful, and somewhat characteristic, crystalline tufts, Plate VIII., fig. 2.
3. $\frac{1}{10,000}$ grain: an immediate cloudiness, and in a few moments crystals appear; after a little time there is a quite good crystalline precipitate, the crystals having the forms just illustrated.
4. $\frac{1}{40,000}$ grain: if only a very minute trace of the reagent be em-

ployed, the mixture soon becomes opalescent, and after a little time, especially when examined by the microscope, yields a very satisfactory deposit of crystalline needles. This precipitate fails to appear in the presence of even very slight excess of the reagent.

If a drop of an aqueous solution of a salt of narcotine be exposed to the *vapor* of ammonia, it soon becomes covered with a white crystalline film, even when it contains only the 1–5000th of its weight of the alkaloid.

2. *Sulphuric Acid and Potassium Nitrate.*

If a solution of narcotine or of any of its salts be evaporated to dryness, the residue dissolved in a small quantity of concentrated sulphuric acid, and then a small crystal of potassium nitrate or a trace of free nitric acid be stirred in the mixture, the latter quickly acquires a deep blood-red color, even if only a minute quantity of the alkaloid be present. This color is discharged by large excess of free nitric acid.

1. $\frac{1}{100}$ grain of narcotine, when dissolved in a single drop of the concentrated acid, and a small crystal of nitre added, yields a deep red coloration. If the nitre be first dissolved in the acid and the mixture then allowed to flow over the narcotine deposit, the latter immediately assumes a deep red color, and slowly dissolves to a solution of the same hue.
2. $\frac{1}{1000}$ grain: if the acid mixture be flowed over the deposit, the latter becomes blood-red, and soon dissolves to a yellow solution.
3. $\frac{1}{10,000}$ grain: the deposit acquires a red color, and very soon dissolves to a faintly yellow solution.

This is one of the most characteristic tests yet known for the detection of narcotine. Under its action the true nature of the precipitate produced by the caustic alkalies or their carbonates may be fully established. For this purpose the precipitate is washed, dried, then dissolved in a drop of sulphuric acid, and a small crystal of nitre stirred in the solution.

When a solution of narcotine in concentrated sulphuric acid is stirred with a very small crystal of *potassium dichromate*, the fluid acquires a beautiful wine color, which remains unchanged for many days. If, however, an excess of the potassium salt be used, the liquid passes through several colors, and ultimately becomes either

green or blue, the final color depending upon the relative amount of the salt employed. The permanent color is readily obtained by stirring the potassium salt in the acid solution until it imparts the desired tint, and then removing the crystal from the mixture. The color may thus be obtained from even a very minute quantity of the alkaloid.

3. *Potassium Acetate.*

A solution of potassium acetate produces in aqueous solutions of salts of narcotine a white precipitate of the acetate of narcotine, which is insoluble in large excess of the precipitant, but readily soluble in most free acids, and in excess of the narcotine solution. If, therefore, the solution contain a free acid, or if the reagent be not added in excess, the mixture may fail to yield a precipitate. The formation of the precipitate from dilute solutions is much facilitated by stirring the mixture.

1. $\frac{1}{100}$ grain of narcotine, in one grain of water, yields a very copious, amorphous deposit, which after a time becomes converted into beautiful groups of crystals, Plate VIII., fig. 3.
2. $\frac{1}{1000}$ grain: an immediate cloudiness, and soon a quite good crystalline deposit.
3. $\frac{1}{5000}$ grain yields after a little time a good deposit of crystalline needles.
4. $\frac{1}{10,000}$ grain: after a few minutes crystals appear.
5. $\frac{1}{20,000}$ grain: after several minutes crystalline needles appear along the edge of the drop, and after a time there is a very satisfactory deposit.

The same precipitate is thrown down from solutions of salts of narcotine by other acetates, such as the acetate of barium, of zinc, and of lead; but the reactions of these, especially the last-mentioned, are not quite so delicate as that of the potassium salt.

The production of a precipitate by the neutral alkali acetates is rather characteristic of narcotine, since it is the only substance, except solutions of salts of silver and mercurous compounds, with which they produce a precipitate, at least in the form of an acetate. In solutions containing silver or mercury, however, the reagent fails to produce a precipitate unless the solution be quite concentrated and a corresponding solution of the reagent be employed.

As the acetates thus serve for the detection of narcotine, so, on the other hand, solutions of salts of the alkaloid serve for the pre-

cipitation of combined acetic acid, for which heretofore we had no ready precipitant. However, as the acetate of narcotine is readily soluble in excess of a soluble salt of the alkaloid, the latter is not so delicate a test for the acetates as these are for narcotine.

4. *Potassium Chromate.*

This reagent throws down from aqueous solutions of salts of narcotine a yellow, amorphous precipitate, which after a time becomes crystalline. The precipitate is readily soluble in acids, even acetic acid.

1. $\frac{1}{100}$ grain of narcotine, in one grain of water, yields a very copious deposit, which slowly assumes the crystalline form.
2. $\frac{1}{1000}$ grain: a quite good precipitate, which soon yields crystalline tufts of the same form as produced by the caustic alkalies (Plate VIII., fig. 2).
3. $\frac{1}{5000}$ grain: much the same as 2. The formation of the crystals is much facilitated by stirring the mixture.
4. $\frac{1}{10,000}$ grain yields in a very little time, especially by stirring, a good crystalline deposit.
5. $\frac{1}{25,000}$ grain: after a few minutes a very satisfactory deposit of crystalline needles and tufts.

The forms of the crystals produced by this reagent are somewhat peculiar to solutions of narcotine.

Potassium dichromate produces in somewhat strong solutions of salts of the alkaloid a yellow, amorphous precipitate, which after a time becomes granular. One grain of a 1–100th solution of the alkaloid yields a copious deposit; and a similar quantity of a 1–500th solution a quite fair, light yellow precipitate; but a 1–1000th solution fails to yield any visible change.

5. *Potassium Sulphocyanide.*

This reagent occasions in solutions of salts of narcotine a white precipitate, which is insoluble in the alkalies, but readily soluble in acids, even acetic acid.

1. $\frac{1}{100}$ grain of narcotine yields a very copious deposit, which soon becomes a mass of crystals of the same form as those produced by the caustic alkalies.
2. $\frac{1}{1000}$ grain: an immediate precipitate, which soon becomes crystalline.

3. $\frac{1}{10,000}$ grain: after a little time, especially if the mixture be stirred with a glass rod, it yields a very satisfactory crystalline deposit.
4. $\frac{1}{25,000}$ grain: after a time a quite satisfactory deposit of crystalline needles.

This reagent produces no precipitate in solutions of salts of morphine.

6. *Auric Chloride.*

Trichloride of gold produces in solutions of salts of narcotine a bright yellow, amorphous precipitate, the color of which is permanent, even upon the addition of caustic potash: in this respect narcotine differs from morphine. Upon heating the mixture the precipitate dissolves, but it is reproduced as the solution cools. The precipitate is but very sparingly soluble in large excess of acetic acid.

1. $\frac{1}{100}$ grain of narcotine, in one grain of water, yields a very copious precipitate.
2. $\frac{1}{1000}$ grain: a very good deposit, which is insoluble in several drops of a strong solution of potassium hydrate.
3. $\frac{1}{10,000}$ grain yields a very satisfactory precipitate.
4. $\frac{1}{20,000}$ grain: after a little time a quite perceptible deposit.
5. $\frac{1}{40,000}$ grain yields a perceptible turbidity.

7. *Iodine in Potassium Iodide.*

A solution of iodine in potassium iodide throws down from solutions of salts of narcotine a reddish-brown, amorphous precipitate, which is nearly insoluble in the caustic alkalies, and only very sparingly soluble in acetic acid.

1. $\frac{1}{100}$ grain of narcotine yields a very copious deposit.
2. $\frac{1}{1000}$ grain: a copious precipitate.
3. $\frac{1}{10,000}$ grain yields a quite good precipitate, which is readily soluble to a clear solution in potassium hydrate.
4. $\frac{1}{50,000}$ grain: a brownish-yellow deposit.
5. $\frac{1}{100,000}$ grain yields a very perceptible turbidity.

8. *Bromine in Bromohydric Acid.*

A solution of bromohydric acid saturated with bromine produces in solutions of salts of narcotine a bright yellow, amorphous precipitate, which is insoluble in large excess of the precipitant, and only sparingly soluble in acetic acid. Upon the addition of potassium

hydrate, the precipitate acquires a white color, except when produced from very dilute solutions, when it dissolves to a clear liquid.

1. $\frac{1}{100}$ grain of narcotine yields a very copious precipitate, which after a time dissolves, but it is reproduced upon further addition of the reagent.
2. $\frac{1}{1000}$ grain: a copious precipitate, which is soluble in potassium hydrate, but is almost immediately replaced by a white deposit.
3. $\frac{1}{10,000}$ grain: a quite good deposit, which, when dissolved in potassium hydrate, yields a slight, white precipitate.
4. $\frac{1}{50,000}$ grain yields a quite distinct, yellowish precipitate.
5. $\frac{1}{100,000}$ grain: a quite distinct cloudiness.

9. *Potassium Ferrocyanide.*

This reagent produces in aqueous solutions of salts of narcotine a dirty-white, amorphous precipitate, which is very readily soluble in acetic acid, but insoluble in large excess of the precipitant.

1. $\frac{1}{100}$ grain of narcotine, in one grain of water, yields a quite copious deposit.
2. $\frac{1}{1000}$ grain: a very good precipitate.
3. $\frac{1}{10,000}$ grain yields a quite strong turbidity.

Potassium ferricyanide throws down from quite strong solutions of narcotine a yellow, amorphous precipitate, which is readily soluble in excess of the precipitant and in acetic acid.

10. *Picric Acid.*

An alcoholic solution of picric acid throws down from solutions of salts of narcotine a bright yellow, amorphous precipitate, which is slowly soluble in large excess of the precipitant, and also in large excess of acetic acid.

1. $\frac{1}{100}$ grain of narcotine yields a very copious precipitate, which remains amorphous.
2. $\frac{1}{1000}$ grain: a very good deposit.
3. $\frac{1}{10,000}$ grain yields a quite obvious precipitate.

Platinic chloride produces in somewhat strong solutions of salts of narcotine a light yellow, amorphous precipitate, which is sparingly soluble in acetic acid. One grain of a 1–100th solution of the alkaloid yields a very copious precipitate, and the same quantity of a 1–1000th solution, a quite fair deposit; but a 1–2500th solution

yields no indications. *Palladium chloride* produces similar results. *Tannic acid* and *corrosive sublimate* throw down from concentrated solutions of the alkaloid white, amorphous precipitates.

When somewhat strong solutions of salts of narcotine are treated with a stream of *chlorine gas*, the liquid quickly assumes a yellow color, which soon changes to reddish-brown; on now adding a solution of ammonia, the mixture acquires a deep brown color. Ten grains of a 1–100th solution of the alkaloid will yield these results. A similar quantity of a 1–1000th solution, when treated with the gas, acquires a distinct yellow tint, which is changed to reddish-brown by ammonia. In these reactions narcotine closely resembles morphine.

V. Codeine.

History.—Codeine, or codeia, as it is frequently called, was first discovered, in 1832, by M. Robiquet. It exists in opium in combination with meconic acid, and usually forms considerably less than one per cent. of the crude drug. The formula for codeine, in its anhydrous state, according to Gerhardt, is $C_{18}H_{21}NO_3$; in its crystalline form, it usually contains one molecule of water of crystallization. It has a bitter taste and strong alkaline properties, quickly restoring the blue color of reddened litmus-paper.

Preparation.—Codeine may be obtained, according to Dr. Gregory, by concentrating the mother-liquor from which morphine has been precipitated, when, after a time, a mixture of the hydrochlorides of codeine and morphine will be deposited. This deposit is dissolved in a little hot water, and the solution treated with excess of potassium hydrate, which precipitates the codeine, partly in the form of crystals and partly as a viscid mass, which soon becomes solid and crystalline; at the same time, most of the morphine present remains in solution in the alkaline liquid. The precipitate is then treated with ether or with water, either of which will dissolve the codeine, while any morphine present will remain undissolved. The ethereal solution, upon spontaneous evaporation, leaves the alkaloid in the form of beautiful anhydrous prisms; while the aqueous solution deposits it in the form of octahedral crystals, containing one molecule of water of crystallization.

Physiological Effects.—The statements in regard to the effects of codeine when taken into the stomach have been quite contradictory.

According to the results of some observers, it has strong narcotic properties, similar to those of morphine, only that it has to be given in larger quantity, and never induces the unpleasant after-effects so frequently witnessed in the administration of that alkaloid. Dr. Gregory observed that in some instances it excited a sense of intense itching of the entire skin, and states that probably the itching caused in some persons by opium and some of the salts of morphine may be due to the action of codeine, this substance being not unfrequently present in some of the preparations of morphine. On the other hand, other observers were led to conclude that codeine was nearly or entirely destitute of narcotic properties. Five grains of codeine, taken by Dr. S. Weir Mitchell, caused slight giddiness and nausea, with some cerebral heaviness. Dr. Wood states that he has given it in doses of eight grains per day without any marked effect.

Chemical Properties.—Codeine is a white, crystallizable, and strongly basic substance, precipitating the oxides of many of the metals from solutions of their salts, but in its turn being precipitated by the caustic alkalies. It is readily distinguished from morphine by not striking a blue color with a ferric salt. When heated, it first parts with its water of crystallization, and at about 120° C. (248° F.) fuses to a colorless liquid, which at higher temperatures takes fire, burning with the evolution of dense fumes.

Codeine completely neutralizes diluted acids, combining with them to form *salts*, most of which are readily crystallizable. Concentrated *sulphuric acid* slowly dissolves the pure alkaloid without change of color; if a solution of this kind be heated on a water-bath, it acquires a beautiful purple color, even when only a minute quantity of the alkaloid is present: this result, however, is somewhat influenced by the amount of acid and heat employed. A small crystal of *potassium nitrate* stirred in the cold acid solution yields a faint greenish, then reddish, coloration; while a crystal of potassium dichromate yields a green color, due to the formation of sesquioxide of chromium. Concentrated *nitric acid*, it is said, produces no change of color with codeine; but the few samples we have examined became more or less orange-yellow, and dissolved to a yellow solution, when treated with this acid, especially when a not inconsiderable quantity of the alkaloid was employed. Similar results have also been obtained by various other observers. *Stannous chloride* added to the nitric acid solution causes it to undergo little

or no change. Hydrochloric acid readily dissolves the alkaloid to a colorless solution, which remains unchanged upon the application of heat.

When excess of finely-powdered codeine is digested with pure *water* at the ordinary temperature, with frequent agitation, for twenty-four hours, the solution then filtered, and the filtrate evaporated to dryness, it leaves a crystalline residue indicating that one part of the alkaloid had dissolved in 128 parts of the fluid. It is much more freely soluble in hot water, from which, however, much of the excess separates as the solution cools. *Absolute ether*, under the foregoing conditions, dissolves one part of the alkaloid in 55 parts of the liquid. *Chloroform*, under similar conditions, takes up one part in 21.5 parts of fluid. The alkaloid is also freely soluble in *alcohol*, and somewhat soluble in solutions of the caustic alkalies, but less so than in pure water. The *salts* of codeine are, for the most part, readily soluble in water, and in alcohol; but they are nearly or altogether insoluble in ether, and in chloroform.

Aqueous solutions of codeine, when not too dilute, have a strongly alkaline reaction and a very bitter taste. The alkaloid may be extracted from its aqueous solution by agitation with *ether;* but, as codeine is not very much less soluble in water than in ether, repeated agitations with the latter are required for the complete separation of the alkaloid. It is much more readily extracted by *chloroform*. By either of these liquids it may be separated from morphine. The alkaloid may, of course, be extracted in a similar manner from aqueous solutions of its salts, by first treating them with slight excess of a free mineral alkali.

The codeine employed in the following investigations was prepared by E. Merck, of Darmstadt: it was in the form of large, colorless crystals, and apparently perfectly pure. Its solutions were prepared in the form of the acetate. The fractions indicate the fractional part of a grain of the pure alkaloid in solution in one grain of water; and, unless otherwise stated, the results refer to the behavior of one grain of the solution.

1. *The Caustic Alkalies.*

The fixed caustic alkalies and ammonia throw down from concentrated aqueous solutions of salts of codeine a white, amorphous precipitate of the pure alkaloid, which is readily soluble in free acids.

One grain of a 1–100th solution of the alkaloid yields a quite good deposit, which remains amorphous. On account of the solubility of codeine in water, solutions but little more dilute than that just mentioned fail to yield a precipitate with either of these reagents.

Since the alkaloid is less soluble in alkaline solutions than in pure water, it is partly precipitated from its pure aqueous solutions, when not too dilute, by the caustic alkalies.

2. *Iodine in Potassium Iodide.*

A solution of iodine in potassium iodide produces in solutions of salts of codeine a reddish-brown precipitate, which is readily soluble to a colorless solution in potassium hydrate; it is also soluble in acetic acid.

1. $\frac{1}{100}$ grain of codeine, in one grain of water, yields a very copious precipitate, which after a time becomes more or less crystalline, Plate VIII., fig. 4. The precipitate is readily soluble in alcohol, from which after a time it separates in the form of crystalline plates, Plate VIII., fig. 5, which are especially beautiful under polarized light. Solutions but little more dilute than this fail to yield crystals.
2. $\frac{1}{1000}$ grain yields a copious deposit.
3. $\frac{1}{10,000}$ grain: a very good, reddish-yellow precipitate.
4. $\frac{1}{50,000}$ grain: a yellowish deposit.
5. $\frac{1}{100,000}$ grain: a quite perceptible precipitate.
6. $\frac{1}{500,000}$ grain yields a distinct turbidity.

This reagent also produces crystalline precipitates with some of the other opium principles; but the deposits produced by the reagent from most other substances remain amorphous.

3. *Bromine in Bromohydric Acid.*

A solution of bromohydric acid saturated with bromine throws down from solutions of salts of codeine a yellow, amorphous precipitate, which after a time dissolves, but it is reproduced upon further addition of the reagent.

1. $\frac{1}{100}$ grain of codeine yields a very copious, bright yellow deposit.
2. $\frac{1}{1000}$ grain: a copious precipitate.
3. $\frac{1}{10,000}$ grain; a fair, yellow deposit.
4. $\frac{1}{25,000}$ grain yields a quite perceptible cloudiness.

The reaction of this reagent is common to solutions of most of the alkaloids, and also to other organic principles.

4. *Potassium Sulphocyanide.*

This reagent occasions in somewhat strong solutions of salts of codeine a white crystalline precipitate of the sulphocyanide of codeine, which, according to Anderson, has the composition $C_{18}H_{21}NO_3,HCNS$. The precipitate is readily soluble in acetic acid.

1. $\frac{1}{100}$ grain of codeine: after some minutes crystalline needles begin to separate, and after a little time there is a copious crystalline deposit, Plate VIII., fig. 6. If the mixture be stirred, it immediately yields crystals, and very soon the drop becomes a mass of crystalline groups.
2. $\frac{1}{500}$ grain: on stirring the mixture, crystals soon appear, and after a time there is a very satisfactory deposit.

This reagent also produces crystalline precipitates with solutions of several other alkaloids.

5. *Potassium Dichromate.*

Potassium dichromate produces in quite strong solutions of salts of codeine a yellow crystalline precipitate, which is readily soluble in acetic acid. Very concentrated solutions of the alkaloid yield beautiful groups of bold, red crystals.

One grain of a 1–100th solution yields no immediate precipitate, but, after standing some time, crystalline tufts separate, and the mixture ultimately becomes a nearly solid mass of crystals, Plate IX., fig. 1. The formation of the precipitate is much facilitated by stirring the mixture.

Potassium chromate produces with very strong solutions of the alkaloid a yellow precipitate of crystalline plates and prisms.

6. *Auric Chloride.*

This reagent throws down from solutions of salts of codeine a reddish-brown amorphous precipitate, which when treated with caustic potash yields a dark-bluish mixture.

1. $\frac{1}{100}$ grain of codeine yields a very copious precipitate: after standing some time, the supernatant fluid acquires a bluish color.

2. $\frac{1}{1000}$ grain yields a very good, yellow deposit.
3. $\frac{1}{5000}$ grain yields a very distinct cloudiness.

7. *Platinic Chloride.*

This reagent precipitates from strong solutions of salts of codeine a yellow, amorphous deposit, which is readily soluble in acetic acid, but unchanged by caustic potash.

1. $\frac{1}{100}$ grain of codeine yields a copious deposit, which after a time becomes more or less granular.
2. $\frac{1}{500}$ grain yields after several minutes a partly granular precipitate.

8. *Picric Acid.*

An alcoholic solution of picric acid produces in solutions of salts of codeine a bright yellow, amorphous precipitate.

1. $\frac{1}{100}$ grain of codeine yields a very copious deposit.
2. $\frac{1}{1000}$ grain: a quite good precipitate.
3. $\frac{1}{2500}$ grain yields after a little time a quite distinct cloudiness.

9. *Nitric Acid and Potassium Hydrate.*

When a small quantity of codeine, in its solid state, is added to a drop of concentrated nitric acid, it dissolves with the evolution of nitrous fumes, yielding an orange-yellow solution, which, when evaporated to dryness on a water-bath, leaves a yellow residue. If this residue be treated with a drop of caustic potash, it acquires a beautiful orange color, and partially dissolves to a solution of the same hue, which is permanent.

1. $\frac{1}{100}$ grain of codeine yields the results just described.
2. $\frac{1}{1000}$ grain: the nitric acid solution leaves a slightly yellow residue, which with caustic potash yields a good orange-colored mixture.
3. $\frac{1}{10,000}$ grain: the slightly yellow residue left by the acid is but little changed by the potassium compound; but if this mixture be evaporated, it leaves a yellowish-orange deposit, mixed with crystals of potassium nitrate: a drop of water readily dissolves these crystals, and yields a yellow-orange mixture, the color of which is permanent.

Potassium iodide produces in concentrated solutions of salts of

codeine, especially upon stirring the mixture, a crystalline precipitate of tufts of needles, Plate IX., fig. 2.

Corrosive sublimate, potassium ferro- and ferri-cyanide, copper sulphate, and silver nitrate produce no precipitate, at least immediately, in a 1–100th solution of salts of codeine.

VI. Narceine.

History.—Narceine, which is said to form from six to twelve per cent. of Smyrna opium, was discovered, in 1832, by Pelletier. Its formula, according to Dr. Anderson, is $C_{23}H_{29}NO_9$. It seems to be a neutral substance, yet it will unite with acids to form salts, all of which have an acid reaction. The statements of observers in regard to the constitution and properties of narceine have been very conflicting, and it is probable that two or perhaps three different substances have been described under this name.

Preparation.—This substance may be obtained, according to Dr. Anderson (*Quart. Jour. Chem. Soc.*, v. 257), from the mother-liquor of hydrochloride of morphine by diluting it with water, filtering, and then adding ammonia as long as a precipitate is produced. Narceine and meconin remain in solution, while narcotine, resin, and small quantities of papaverine and thebaine are deposited. The filtered liquid is treated with excess of lead acetate, the dirty-brown precipitate produced removed by a filter, the excess of lead separated from the filtrate by sulphuric acid, and the liquid saturated with ammonia, then evaporated at a moderate temperature to a syrup, when it is allowed to stand some days. The precipitate then formed is collected on a cloth and washed with water, then boiled with a large quantity of water and the hot solution filtered. On cooling, the liquid becomes filled with fine silky crystals of narceine, which are separated from traces of calcium sulphate by solution in alcohol, and further purified by boiling with animal charcoal and recrystallization from water.

Physiological Effects.—Experiments upon inferior animals indicate narceine to be an inert substance.

Chemical Properties.—Narceine crystallizes in beautiful, colorless, delicate needles, which when dry form an exceedingly light, spongy mass. It is unchanged by persalts of iron. At a moderate heat it fuses to a clear liquid, and at higher temperatures burns like a resin.

The narceine used in the present investigations was prepared by E. Merck: it was in the form of very delicate, colorless, silky needles.

Concentrated *sulphuric acid* causes the alkaloid to assume a reddish-brown color, and dissolves it to a reddish or yellowish-red solution, which upon the application of a moderate heat acquires an intense red color, and at higher temperatures darkens. These results, however, are much influenced by the amount of acid and heat employed. In no instance, with the single specimen examined, did we obtain the green color described by Anderson (*Quart. Jour. Chem. Soc.*, v. 259), nor, with the diluted acid, the blue color obtained by other observers. A crystal of potassium nitrate stirred in the cold acid solution yields a reddish-brown, violet, or purple coloration, according to the relative quantities of the different substances present: the color is discharged by heat. Potassium dichromate produces with the acid solution a dirty-red color, which on the application of heat is changed to green, due to the production of sesquioxide of chromium.

When treated with concentrated *nitric acid*, narceine assumes an orange-red color and dissolves to a more or less yellow solution, which suffers little or no change by a moderate heat. The solution is unaffected by stannous chloride, even upon the application of heat. The sample under consideration, when dropped into concentrated hydrochloric acid, became blue, and dissolved to a perfectly colorless solution. Pelletier described this reaction as characteristic of narceine, while Anderson failed to obtain a blue color from samples which he considered pure.

When excess of narceine is digested, with frequent agitation, for twenty-four hours in *water* at the ordinary temperature, it requires 1660 parts of the liquid for solution. It is much more soluble in hot water, from which the excess slowly separates as the solution cools. One part of the alkaloid dissolves in five hundred parts of water as soon as the mixture is brought to the boiling temperature; this solution may then be exposed for half an hour or longer to a temperature of 15.5° C. (60° F.) before crystals begin to separate. A concentrated aqueous solution of narceine has no action upon reddened litmus. *Absolute ether*, under the foregoing conditions, dissolved one part of narceine in 4066 parts of the liquid. *Chloroform*, under similar circumstances, dissolved one part in 7950 parts of

liquid. It is much more soluble in alcohol than in water, and is also somewhat soluble in dilute solutions of the caustic alkalies.

In the following investigations, the 1–100th solutions were obtained by the aid of hydrochloric acid and a gentle heat; the more dilute solutions were prepared by dissolving the narceine, when necessary by the aid of heat, directly in distilled water. A 1–100th solution of narceine in the form of hydrochloride, unless maintained at a gentle temperature, soon becomes filled with a net-work of long, delicate, crystalline needles.

1. *Iodine in Potassium Iodide.*

A solution of iodine in potassium iodide produces in solution of narceine a reddish-yellow precipitate, which almost immediately becomes crystalline. The precipitate is slowly soluble in large excess of acetic acid.

1. $\frac{1}{100}$ grain of narceine, in one grain of water, yields a very copious deposit, which very soon becomes a mass of crystalline needles and tufts; at the same time the mixture acquires a blue color. The precipitate is readily soluble in alcohol, from which it soon again separates in the crystalline form.
2. $\frac{1}{1000}$ grain yields a copious precipitate, which soon changes to exceedingly delicate crystalline tufts, Plate IX., fig. 3. After a time the mixture acquires a more or less blue color.
3. $\frac{1}{5000}$ grain after a time yields some few crystalline tufts, of the forms just illustrated.

The production of these crystalline tufts is quite peculiar to solutions of narceine.

2. *Bromine in Bromohydric Acid.*

A solution of bromine in bromohydric acid throws down from solutions of narceine a bright yellow, amorphous precipitate, which after a time dissolves, but is reproduced upon further addition of the reagent. The precipitate is soluble in acetic acid and in alcohol.

1. $\frac{1}{100}$ grain of narceine, in one grain of water, yields a very copious precipitate.
2. $\frac{1}{1000}$ grain: a copious deposit.
3. $\frac{1}{10,000}$ grain yields after a very little time a quite fair, yellow precipitate.

3. *Auric Chloride.*

This reagent occasions in solutions of narceine a yellow, flocculent precipitate, which remains unchanged in color. The precipitate is soluble in the mixture upon the application of heat, and is reproduced unchanged as the solution cools. It is readily soluble to a clear solution in potassium hydrate.

1. $\frac{1}{100}$ grain of narceine yields a very copious deposit.
2. $\frac{1}{1000}$ grain: a very good precipitate.
3. $\frac{1}{10,000}$ grain yields after a little time a perceptible turbidity, which soon becomes quite well marked.

4. *Platinic Chloride.*

This reagent precipitates from solutions of narceine a yellow, flocculent deposit, which is readily soluble in acids. After a time the precipitate yields granules and crystalline needles.

1. $\frac{1}{100}$ grain of narceine yields a very good deposit.
2. $\frac{1}{500}$ grain: a very fair precipitate.
3. $\frac{1}{1000}$ grain: no indication.

5. *Picric Acid.*

An alcoholic solution of picric acid causes in solutions of narceine a yellow, amorphous precipitate, which is readily soluble in acetic acid.

1. $\frac{1}{100}$ grain of narceine yields a copious deposit.
2. $\frac{1}{1000}$ grain: a good precipitate.
3. $\frac{1}{5000}$ grain yields after a little time a quite satisfactory deposit.

6. *Potassium Dichromate.*

This reagent produces in strong solutions of narceine a yellow, amorphous precipitate, which soon becomes crystalline.

1. $\frac{1}{100}$ grain of narceine yields a very copious precipitate, which almost immediately becomes a mass of crystals.
2. $\frac{1}{500}$ grain yields a very good crystalline deposit, Plate IX., fig. 4.

Potassium chromate produces in solutions of the alkaloid much the same results as the dichromate.

Potassium iodide, potassium sulphocyanide, corrosive sublimate,

potassium ferro- and ferri-cyanide, produce no precipitate in even saturated aqueous solutions of narceine.

VII. Opianyl.

History.—Opianyl, or Meconine, as it was formerly named, was discovered, in 1826, by M. Dublanc, but first described by M. Couerbe, in 1832. It is a neutral crystallizable substance, and forms less than one per cent. of opium. Its formula, as first determined by Couerbe, and afterward confirmed both by Regnault and by Anderson, is $C_{10}H_{10}O_4$. It therefore differs from the alkaloids in not containing nitrogen.

Preparation.—Opianyl may be obtained from the mother-liquor from which narceine has been prepared by agitating it with successive portions of *ether*, as long as this liquid becomes colored. The united ethereal solutions are then evaporated, and the brown syrup treated with dilute hydrochloric acid, which dissolves the papaverine, while the opianyl, together with some resin, remains. The opianyl is then crystallized several times from boiling water, with the addition of animal charcoal, when it finally separates in colorless needles. It may also be obtained by acting upon narcotine with nitric acid.

Physiological Effects.—From the few experiments made with this substance, it would seem to be inert.

Chemical Properties.—Opianyl readily crystallizes in the form of long, colorless, six-sided prisms, or as delicate needles; it has a somewhat bitter taste. At a moderate heat, it fuses to a colorless liquid, which upon cooling solidifies to a radiated crystalline mass; at higher temperatures, it is dissipated in the form of white fumes. When cautiously heated in a glass tube, it sublimes in beautiful crystals (Anderson). According to Dr. Guy, opianyl fuses at 48.8° C. (120° F.), and vaporizes at 82.2° C. (180° F.). Although a perfectly neutral body, opianyl is soluble in acids.

The following observations are based upon the examination of a single specimen of opianyl, prepared by E. Merck. It was in the form of delicate, snow-white crystals.

Concentrated *sulphuric acid* dissolves it to a colorless solution, which when heated acquires either a beautiful blue or purple color, the hue depending upon the relative quantity of acid employed (see

post); the cooled mixture, upon the addition of water, becomes reddish-brown and yields a brownish precipitate. *Nitric acid* also dissolves it to a colorless solution, which on being heated acquires a more or less yellow color, and on evaporation leaves a colorless crystalline residue. It is also soluble in concentrated hydrochloric acid without change of color, even upon the application of heat.

When excess of opianyl is digested in *water* for several hours, with frequent agitation, at a temperature of about 15.5° C. (60° F.), one part dissolves in 515 parts of the liquid. According to Couerbe, it dissolves in 265 parts of cold water; while Anderson states that at 15.5° C. (60° F.) it requires 700 parts of this liquid for solution. It is much more freely soluble in hot water, but much of the excess separates in its crystalline state as soon as the solution begins to cool. When excess of opianyl is boiled with water, it melts under the liquid; yet, according to Anderson, when in its dry state, it requires a temperature of 110° C. (230° F.) for its fusion. *Absolute ether*, when in contact with excess of opianyl for several hours at the ordinary temperature, dissolves one part in 136 parts of the liquid. *Chloroform* dissolves it in all proportions. It is also readily soluble in *alcohol;* but it is not more soluble in solutions of the caustic alkalies than in pure water.

In the following investigations, the opianyl was dissolved, when necessary by the aid of a very gentle heat, in pure water.

1. *Iodine in Potassium Iodide.*

A solution of iodine in potassium iodide produces in aqueous solutions of opianyl a yellowish-brown, amorphous precipitate, which quickly becomes quite dark brown, and then changes to a mass of yellow crystals, which in their dry state resemble spangles of gold-dust. The precipitate is readily soluble in alcohol.

1. $\frac{1}{500}$ grain of opianyl, in one grain of water, yields a very copious precipitate, which very soon becomes converted into yellow crystals, Plate IX., fig. 5.
2. $\frac{1}{1000}$ grain: a good, yellowish-brown deposit, which soon darkens.
3. $\frac{1}{2500}$ grain yields after a little time a slight cloudiness, followed by the precipitation of dark-colored granules.

The reaction of this reagent is quite peculiar to solutions of opianyl.

2. *Bromine in Bromohydric Acid.*

This reagent precipitates from solutions of opianyl a deposit of short needles, and groups of hair-like crystals. The precipitate is insoluble in acetic acid, and but slowly soluble in large excess of alcohol.

1. $\frac{1}{500}$ grain: after a few moments crystals begin to form, and soon there is a quite copious deposit, Plate IX., fig. 6; after a time the mixture becomes a colorless mass of crystals.
2. $\frac{1}{1000}$ grain: in a very little while a quite good crystalline deposit.
3. $\frac{1}{2500}$ grain yields after a little time a very satisfactory crystalline precipitate.

The production of this crystalline precipitate is quite characteristic of opianyl.

3. *Sulphuric Acid and Heat.*

When a small quantity of opianyl in its solid state is heated with a very minute portion of concentrated sulphuric acid, it yields an intense blue color, which, as the heat is increased, changes to purple; when a larger quantity of acid is employed, the heated mixture acquires a transient blue color, which passes to purple; while with a still larger quantity the mixture, when heated, assumes at once a beautiful purple color. This experiment may be performed in a thin, annealed watch-glass.

1. $\frac{1}{500}$ grain of opianyl, when moistened with a very small quantity of the acid, and heated, yields an intense blue coloration.
2. $\frac{1}{1000}$ grain: much the same as 1. For the success of this reaction it is essential that the least possible quantity of acid be employed. This is best attained by touching the deposit with a glass rod moistened with the acid; the mixture is then heated over the flame of a spirit-lamp, until it begins to assume a blue color,—which does not usually occur until vapors of the acid are evolved,—when the heat is withdrawn.
3. $\frac{1}{10,000}$ grain, when treated as just described, yields very satisfactory results.
4. $\frac{1}{25,000}$ grain: if the deposit be not distributed over a large space, it yields a very distinct blue coloration.

With a very small quantity of the acid, a blue color may be

obtained from a much less quantity of opianyl than will yield a purple color with a larger quantity of the acid. The production of this blue coloration is quite characteristic of opianyl. *Narcotine* when heated with a small quantity of sulphuric acid yields a purple mixture, which darkens as the heat is increased. So, also, a sulphuric acid solution of *codeine*, when heated, acquires a purple color.

A sulphuric acid solution of opianyl, when stirred with a few crystals of potassium nitrate, yields a yellow mixture, soon changing to a beautiful scarlet-orange color, which but slowly fades. Almost the least visible quantity of the substance, when treated in this manner with a very small quantity of the acid and nitre, yields very satisfactory results. On heating the mixture, the orange color is changed to yellow. In these reactions opianyl somewhat resembles narcotine.

As opianyl forms no definite combinations with acids or with the metals, it is not precipitated by the ordinary reagents. According to Couerbe, it yields a crystalline precipitate with basic lead acetate; but, like Anderson, we failed to obtain a precipitate by this reagent.

CHAPTER III.

NUX VOMICA, STRYCHNINE, BRUCINE.

I. Nux Vomica.

History and Composition.—Nux vomica is the seed of the *Strychnos nux vomica*, a tree found native in the East Indies and the island of Ceylon. The seeds are flat, nearly round, and something less than an inch in diameter, being slightly concave on one side, and convex on the other, and covered with short, silky, grayish or yellowish hairs, which are attached to an investing membrane and incline towards the circumference of the seed. The seeds are very hard, difficult to pulverize, and when chewed have an intensely bitter taste, but they are destitute of any well-marked odor. In its powdered state nux vomica has a yellowish-gray color, and a peculiar odor, not very unlike that of liquorice.

Nux vomica possesses powerful poisonous properties, due to the presence of the alkaloids *strychnine* and *brucine*, which exist in the seed in combination with a peculiar organic acid, known as strychnic, or igasuric, acid. The seeds also contain, according to the analysis of Pelletier and Caventou, yellow coloring matter, gum, a waxy substance, starch, a concrete oil, woody fibre, and earthy salts. A third alkaloid, under the name of igasurine, was described by M. Desnoix. But, according to W. A. Shenstone (*Jour. Chem. Soc.*, Sept. 1881, 453), the substance thus described is nothing more than impure brucine. The powdered seeds yield their active properties to water, but much more freely to alcohol. Poisoning by this substance has been of quite frequent occurrence.

Symptoms.—The symptoms produced by poisonous doses of nux vomica, or either of its active alkaloids, are very uniform in their nature, and quite peculiar. There is at first a sense of numbness in

the extremities, with more or less trembling of the muscles, and a feeling of great anxiety. These effects are soon succeeded by violent muscular contractions, in which the limbs are extended and perfectly rigid, the head thrown back, the jaws fixed, the face livid, and the respiration apparently suspended. After a little time, varying from a few moments to some minutes, the convulsive paroxysm subsides, and the patient then feels much exhausted, and is usually extremely sensitive to external impressions. This condition, however, is usually of short duration, the convulsions being succeeded by others, which increase in violence, and speedily run to a fatal termination. In some instances death takes place during a paroxysm, but more generally from extreme exhaustion. The intellectual faculties usually remain unaffected, even up to the time of death. The *time* within which the symptoms first manifest themselves is subject to considerable variation, they occurring in some instances almost immediately, and in others being delayed for even more than an hour.

The following case, reported by Mr. Ollier, well illustrates the usual effects of nux vomica. A young woman purposely swallowed, in suspension in water, about three drachms of the powder. When seen about half an hour afterward, she was calm and quite well. But in about ten minutes more she was seized with a convulsive fit, and in a few minutes afterward had another, which was soon succeeded by a third: the duration of these paroxysms was about two minutes each. During the attacks the whole body was extended and rigid, the legs widely separated, the face and hands livid, and the muscles of the former violently convulsed: no pulse or breathing could be perceived. In the intervals she was quite sensible; complained of being sick, and made many attempts to vomit; had incessant thirst, a very quick and feeble pulse, and perspired freely. A fourth attack soon followed, in which the whole body was extended to the utmost and rigidly stiff. She now fell into a state of asphyxia, relaxed her grasp, white foam issued from her mouth, the expression of the countenance became most frightful, and death ensued in about an hour after the poison had been taken. (*London Med. Repository*, xix. 448.)

In a non-fatal case related by Dr. Basedow, of Merseburg, the following symptoms were observed. A young lady took by mistake a tablespoonful of the powdered drug. She was almost instantly deprived of the power of walking, and fell down, but still retained

her consciousness. When first seen by Dr. Basedow, almost immediately afterward, her countenance was pale, and exhibited alternately an expression of indifference and anxiety; the eyes were wide open, and the pupils contracted. The respiration was irregular and short; the pulse irregular and small, and the skin cool. The forearms were constantly in a half-bent position, and the hands and fingers affected with convulsive twitches; but the legs were motionless and rigid, all the muscles being hard and tetanically contracted. The patient had not the slightest pain or sickness; but her breathing became every moment more difficult, and she complained of impending suffocation. An emetic was now administered, and its action followed by the exhibition of small doses of a mixture of oil of turpentine and sulphuric ether. The dyspnœa gradually subsided, and in about six hours after the poison had been taken the tetanic spasms of the muscles of the legs, as well as the convulsive movements of the hands, had ceased, and the respiration was free; but the patient complained of a sense of bruising over the whole body, and pain in the limbs, for some days afterward. (*New York Med. and Phys. Journal*, xxx. 448.)

In some few of the recorded cases of poisoning by this substance, the first symptoms observed were nausea and vomiting; while in others the tetanic symptoms were followed by purging, and inflammation of the stomach and bowels.

Period when Fatal.—In fatal poisoning by *nux vomica*, death usually takes place within a very few hours after the poison has been taken; but life has been prolonged for some days. In a case cited by Dr. Christison, in which a man swallowed an unknown quantity of the powder mixed with beer, death occurred in fifteen minutes after the poison had been taken. (*On Poisons*, 686.) Several instances are related in which death took place in from one to two hours. On the other hand, in a case cited by Orfila (*Toxicologie*, ii. 605), a man swallowed a considerable quantity of the powder, and almost immediately was seized with violent convulsions; yet death did not occur until the fourth day.

Fatal Quantity.—In a case quoted by Dr. Christison, an old woman who was using an *alcoholic extract* of nux vomica for palsy took an overdose of *three grains*, which soon produced violent tetanic spasms, followed by an attack of inflammation of the stomach and intestines, and death on the third day. The quantity of the crude

powder represented by the extract taken in this case is quite uncertain. In another case, *four grains* of the extract taken by a lady, through the mistake of a druggist, caused her death within a few hours. (*Amer. Jour. Pharm.*, July, 1867, 379.) In an instance related by Hoffmann, *thirty grains* of the crude powder, taken in two equally divided doses, caused death. Dr. Taylor mentions two cases, in each of which fifty grains of the powder proved fatal: in one of these, death took place in an hour. (*On Poisons*, 767.) In another instance, two drachms caused death in about two hours.

A boy, aged twelve years, took into his mouth about eight grains of the extract, thinking it was liquorice. Finding it very bitter, he spat out as much as he could. About an hour later, there were some slight twitchings of the muscles, and soon after, well-marked opisthotonos, with an increase of the spasms, and the face was flushed and anxious. The patient was aware of the approach of the spasms, saying, "It's coming;" and there was a sense of impending death, he saying, "Good-by; I'm dying." Under treatment, the boy recovered within a few days. (*Guy's Hosp. Rep.*, xiv. 266.) Recovery has not unfrequently taken place after comparatively large quantities of nux vomica had been swallowed.

Treatment.—The stomach should be emptied as speedily as possible, either by means of the stomach-pump or by the administration of an emetic. Since the poison, when taken in the form of powder, sometimes adheres tenaciously to the walls of the stomach, the use of the pump, or the action of the emetic, should be continued for some time. Various chemical antidotes have been advised, but none of these are reliable. After the contents of the stomach have been evacuated, vegetable astringents, or a solution of iodine in potassium iodide, might be found useful for the purpose of neutralizing any remaining portions of the poison. Other methods of treatment will be referred to hereafter, when considering the antidotes for poisoning by strychnine.

Post-mortem Appearances.—Nux vomica may occasion death without leaving any well-marked morbid change in any part of the body. In Mr. Ollier's case, before cited, in which death took place in an hour, five hours after death the body was as straight and stiff as a statue, so that if one of the hands was moved the whole body moved with it. On dissection, the stomach was found nearly natural, the blood-vessels of the brain congested, and the heart of a pale color,

empty, and flaccid. In another case, in which about an ounce of the poison had been taken and proved rapidly fatal, large quantities of a sanguinolent fluid were found in the cavities of the brain and between its membranes; and the lungs, as well as the heart, were highly gorged with black fluid blood. The stomach was healthy, except a patch of the mucous membrane in the larger curvature of the organ, which was evidently inflamed, and of a deep red color, the intensity diminishing from the circumference to the centre.

In the case cited from Orfila, in which death did not take place until the fourth day, the following appearances were observed forty-eight hours after death. The body was considerably rigid, and of a violet hue. The lateral ventricles of the brain, and the cavity of the arachnoid membrane, contained large quantities of serum; but no appreciable alteration was detected in either the meninges or the cerebral substance. The internal surface of the stomach presented at different points a color which varied from red to deep black; and the duodenum and upper portions of the small intestines were manifestly inflamed. The lungs were gorged with blood; the heart was natural.

Chemical Properties.

The physical properties of nux vomica, when in its solid state, readily distinguish it from all other substances. If a small portion of the powdered seed be moistened with a drop of water, and examined under a low power of the microscope, the broken fibrous hairs may be readily distinguished, they apparently forming a large portion of the powder. The hairs acquire a yellow color upon the addition of a solution of iodine in potassium iodide; when the crude powder is thus treated, it assumes a deep brown color. When touched with a drop of concentrated nitric acid, the powder acquires a deep orange-red color, which is slowly discharged by a solution of stannous chloride. Concentrated sulphuric acid causes it, like most vegetable powders, to assume a brownish, then black color. Hydrochloric acid produces little or no change. When moderately heated, the powder evolves dense, white fumes having a peculiar odor; at higher temperatures it becomes ignited.

When powdered nux vomica is macerated in water or diluted alcohol, the liquid takes up the strychnine and brucine, as salts of their peculiar acid, and more or less coloring matter: this extraction is much facilitated by a moderate heat. The solution thus obtained

has an intensely bitter taste, strikes a red color with nitric acid, and yields a copious reddish-brown precipitate with a solution of iodine in potassium iodide. It acquires a greenish hue when treated with a solution of a ferric salt; ammonio-copper sulphate produces a somewhat similar coloration, and, after a time, a greenish-white precipitate. Tannic acid throws down from the solution a copious, dirty-white precipitate.

It is obvious that there can be no chemical test by which the presence of *nux vomica* as a whole, when in a complex organic mixture, can be directly shown; but this may be inferred by proving the presence of one or more of its peculiar principles. Of these principles, strychnine is usually much the most easy of detection. Since, however, this alkaloid is so frequently met with in its pure state, or that of some of its salts, its mere detection would not, independent of other circumstances, prove the presence of nux vomica. The methods for the separation of strychnine and brucine from organic mixtures of the crude drug are the same as those for their recovery from organic mixtures in general, as will be pointed out hereafter under the special consideration of these alkaloids.

II. Strychnine.

History.—Strychnine, or *strychnia,* was discovered, in 1818, by Pelletier and Caventou, both in the seed of *Strychnos nux vomica* and the *St. Ignatius' bean,* which latter is the seed of the *Strychnos Ignatii.* Thus far it has been found only in five species of the Strychnos genus of plants, and in most of these it is accompanied by brucine. Several of the species of this genus of plants contain neither strychnine nor brucine. The composition of strychnine, in its anhydrous state, according to Regnault, and since confirmed by Nicholson and Abel, is $C_{21}H_{22}N_2O_2$; molecular weight 334. According to most analysts, strychnine forms something less than one-half per cent. by weight of nux vomica; Mr. Horsley, however, states that he obtained about one per cent. of the alkaloid from that substance. From the St. Ignatius' bean Pelletier and Caventou obtained from one to two per cent. of the alkaloid.

Preparation.—Strychnine may be obtained from nux vomica by the following process. The rasped seeds are digested for twenty-four hours in water acidulated with hydrochloric acid, the decoction then strained through linen, the strained liquid concentrated to a

small volume, and then precipitated with milk of lime; the precipitate thus produced is collected on a cloth, washed with cold water, then dried, and the pulverized mass exhausted with successive portions of alcohol until deprived of its bitterness. The mixed alcoholic liquids are concentrated on a water-bath, and then treated with water containing a little sulphuric acid, by which the strychnine will be dissolved in the form of sulphate. This solution is boiled with animal charcoal, filtered, concentrated to a small volume, and the alkaloidal sulphate allowed to separate by crystallization. The crystals may now be dissolved in pure water, and the alkaloid precipitated by slight excess of ammonia, then collected on a filter, washed with cold water, and allowed to dry. As thus obtained, strychnine usually contains more or less brucine.

Mr. Horsley's method for preparing the alkaloid consists in first exhausting powdered nux vomica by repeated extractions with water strongly acidulated with acetic acid. The united acid liquids are then filtered, and the filtrate evaporated to a syrupy consistency. The cooled residue is diluted with water, slight excess of ammonia added, and the mixture allowed to repose for one or two days. Any crystals thus obtained are washed, dried, then redissolved in water containing acetic acid, and the solution filtered. The liquid is now treated with a solution of potassium chromate, by which the alkaloid is precipitated as strychnine chromate. This is collected, washed, then digested in a solution of ammonia, when, the chromic acid uniting with the ammonia, the strychnine separates in its pure state.

Strychnine is one of the most virulent poisons known. It is found in the shops both in its free state and in the form of some of its salts; its principal salts are the sulphate, the hydrochloride, or muriate, and the acetate. The ordinary medicinal dose of strychnine, or of any of its saline combinations, is about one-sixteenth of a grain.

Symptoms.—These are the same in kind as those produced by nux vomica, but they usually manifest themselves even more promptly. The first symptoms are usually a sense of oppression and great anxiety, with quivering and spasmodic movements of the muscles of the extremities. These effects are sooner or later succeeded by violent muscular convulsions, in which the head is thrown back, and the whole body is rigidly stiff, the extremities being extended, the hands firmly clinched, and the feet arched. In this

state, the jaws are usually firmly closed, the eyes prominent, the pupils dilated, the face livid, the expression anxious, and often foam issues from the mouth; the muscles of the chest and diaphragm are also strongly contracted, and the respiration is apparently arrested; the pulse is either very rapid or altogether imperceptible. In a little time, varying from less than a minute to several minutes, this tetanic condition usually entirely disappears, and there is a state of calm. During this state the patient feels extremely weak, usually experiences great thirst, and is sometimes inclined to sleep. After a little time, however, the system again becomes excited, the special senses being exceedingly acute, and frequently there is a sense and declaration of impending death. A second paroxysm may now be induced by very slight causes, or it may appear without any apparent cause. Not unfrequently the patient is perfectly conscious of the approach of the attack, and desires to be held or rubbed. After a succession of attacks, varying from two to several, death takes place either during a paroxysm from asphyxia, or, more frequently, soon after from complete exhaustion. The interval between the paroxysms has varied from a few minutes to more than half an hour. The intellect usually remains clear up to the time of death.

In a case reported by Dr. Blumhardt, in which a young man, for the purpose of self-destruction, swallowed forty grains of strychnine, the following symptoms were observed. The patient soon experienced great anxiety and agitation, and after the lapse of fifteen minutes, an emetic having been administered, but with the effect of producing only slight vomiting, he lay stiff upon his back, with the head somewhat bent backwards; the lower extremities were perfectly stiff, but the upper still free; the countenance was pale and haggard; the pulse quick and contracted. He still spoke with a firm voice and in a collected manner, but trismus was evidently commencing. The attacks soon became more violent, and the spasms extended to the muscles of the chest; the thorax appeared compressed, and the respiration was impeded. The paroxysms were now repeated at intervals of about a minute, for a short time, when the whole body became affected and as stiff as a board. The suffocation was now extreme; the jaws firmly locked together; the upper extremities firmly flexed at the elbow-joints and applied across the chest; the lower extremities extended and stiff, and the soles of the feet concave. By degrees the respiration became

more unequal, and finally ceased; the pulse became imperceptible; the skin of a dusky blue color; the face deep purple; the eyes prominent, and the pupils dilated and insensible. All signs of consciousness soon disappeared, and the patient lay for a few minutes without motion, in a state of universal tetanus. A remission of the convulsions now suddenly manifested itself; the limbs became relaxed, and after a long, deep-drawn inspiration the pulsations of the heart and arteries were again perceptible; consciousness and the power of speech were also restored, but the articulation was imperfect. After about fifteen minutes the patient was again seized with a shivering fit, followed by general tetanus, which soon terminated in a state of asphyxia, and death took place an hour and a half after the poison had been taken. (*American Medical Intelligencer*, ii. 28.)

The following case of recovery is related by Dr. Powel. (*Lancet*, Aug. 1861, 169.) A woman, aged twenty-eight years, took not less than two or three grains of strychnine on an empty stomach. When first seen by the physician, over half an hour afterward, she was lying on her back on the floor, quite sensible; the arms and legs were stretched out to their fullest extent; hands clinched; toes flexed; legs close together, and the body in a state of opisthotonos. The countenance was livid and anxious; the eyes staring and fixed, pupils widely dilated, conjunctivæ highly injected; teeth firmly clinched. The breathing was irregular, and at times almost ceased; skin hot, and bathed in perspiration; pulse rapid and scarcely perceptible. The spasms relaxed at times, but did not entirely cease for one minute. On the slightest touch of the body or legs, or on an attempt to give her drink, she would cry out, "My legs! my legs! hold me! hold me!" then utter a shriek, and quickly relapse into a most violent spasm involving the entire body. Under the administration of chloroform the convulsions became less severe. While under the influence of the anæsthetic, an emetic was administered, and produced some vomiting. For some hours the spasms recurred about every five minutes, but with decreasing severity, and finally the woman fully recovered.

In a few of the reported cases of strychnine poisoning, the first symptom observed was the utterance of a loud cry or shriek; and at least two instances are recorded in which the tetanic symptoms were preceded by vomiting. (Dr. J. St. Clair Gray, *Strychnia*, 1872, 46.) In an instance of the former kind, in which we were recently consulted,

a woman about her ordinary work suddenly exclaimed, *Oh!* and quickly fell, saying her feet had given out; violent tetanic symptoms speedily ensued, followed by death.

The *time* within which the symptoms first manifest themselves in strychnine poisoning has varied from a few minutes to some hours; but they do not often appear much before fifteen minutes, nor are they often delayed much beyond half an hour. In a case reported by Dr. G. F. Barker (*Amer. Jour. Med. Sci.*, Oct. 1864, 399), a young, healthy, married woman had administered to her, with criminal intent, not exceeding six grains of strychnine, and violent symptoms were present in *three minutes* afterward; these were succeeded by several convulsive paroxysms, and death during a paroxysm in thirty minutes after the poison had been taken. In this instance the strychnine was taken in its dry state into the mouth and washed down with water. This is perhaps the most rapid case, in regard to the appearance of the symptoms, yet recorded. In the case of Dr. Warner, of Vermont, who by mistake took, it is believed, something less than half a grain of the poison, well-marked symptoms were present within five minutes, and death occurred in about eighteen minutes. In at least three other cases the symptoms were about equally prompt in appearing.

On the other hand, Dr. H. G. Thomas, of Alliance, Ohio, has reported a case in which a man swallowed *five grains* of strychnine, and *one hour and three-quarters* elapsed before any symptoms manifested themselves; and, under the use of emetics, the patient recovered. One of the most remarkable cases of this kind yet recorded is the following, reported by Dr. T. Anderson. A gentleman took by mistake, believing it to be a salt of morphine, three grains and a half of strychnine, and experienced no particular symptoms until *two hours and a half* afterward, when he suddenly fell backwards; but, on being immediately raised, he was able to walk home, although exceedingly nervous and alarmed. He soon felt better, and in five hours after taking the dose he again took a similar quantity. In less than ten minutes after taking the last dose he was seized with violent tetanic spasms, which continued, with the usual intermissions, for several hours, after which he entirely recovered. (*Amer. Jour. Med. Sci.*, April, 1848, 562.) The form in which the poison is taken, and the condition of the stomach, may to some extent determine the time at which the symptoms first appear; but several instances are re-

corded in which the symptoms were delayed much beyond the ordinary period, even under conditions apparently the most favorable for their development.

It need hardly be remarked that the effects of strychnine may be much modified by the presence of another poison. A case of this kind, in which three grains of strychnine and one drachm of opium were taken and no serious symptoms appeared for nearly twelve hours, has already been mentioned (INTRODUCTION, 39). The following somewhat similar case may also be cited. A young druggist, with suicidal intent, swallowed, at half-past eight o'clock in the evening, between eight and ten grains of nitrate of strychnine in an ounce of bitter-almond water. A little later, he took an additional dose of twelve grains of strychnine. Feeling nothing peculiar, he took at nine o'clock ten grains of acetate of morphine dissolved in an ounce of bitter-almond water, and then lay down in bed. Ten minutes later, to hasten his death, he poured some chloroform on his pillow. Partial insensibility now manifested itself, and continued for about an hour and a half, when he was seized with violent cramps and cessation of respiration, but without pain. Loss of consciousness then supervened, but he soon revived, and had another attack of convulsions. Emetics and tannic acid were now administered; and in two days afterward no trace of the poisoning remained. (*Amer. Jour. Med. Sci.*, Jan. 1863, 259.) Recovery in this case has been ascribed to the fact that the patient, before taking the poison, had partaken freely of a soup made with flour and a species of cranberries. These latter contain tannin, an agent which is said to neutralize strychnine; and the farinaceous matters, by enveloping the poison, may have prevented its absorption. In another case, a young woman having taken about one grain and a half of strychnine, and immediately afterward two ounces of laudanum, symptoms of opium poisoning appeared in four hours; but the effects of the strychnine did not manifest themselves until about *eight hours* after the poison had been taken. Under treatment, the woman entirely recovered. (*Medical Times*, Dec. 1882, 175.)

The *external application* of strychnine may be attended with serious and even fatal consequences. In a case related by Dr. Schuler, something less than the *twelfth of a grain* of pure strychnine was introduced into the corner of the eye of a man affected with amaurosis. In less than three or four minutes the patient's

face became livid, and he was seized with spastic yawnings and vertigo. These symptoms increased, and loss of speech and pulse, with convulsive respiration and violent tetanic shocks, ensued. Death seemed inevitable, but, under the action of remedies, all the symptoms passed off in less than half an hour. (*Amer. Jour. Med. Sci.*, Oct. 1861, 573.)

It was formerly believed that strychnine, when given in frequently repeated small doses, never *accumulates* in the system; but this result has occasionally been observed. Thus, Dr. Dutgher relates a case in which he administered to a middle-aged woman, affected with partial paralysis of the muscles of deglutition, the fifth of a grain of strychnine daily, in divided doses, for nine days, without any effect other than a gradual improvement of the paralytic condition. But on the morning of the tenth day the patient was seized with pretty severe tetanic spasms, which continued, at intervals of about twenty minutes, for several hours, when they ceased, and the patient recovered without any vestige of the paralysis remaining. (*Med. and Surg. Reporter*, Philadelphia, July, 1865, 2.) It will be observed that the entire quantity of strychnine taken in this case did not exceed two grains.

A fatal case apparently of this kind was communicated, by Mr. Cooper, to the late Dr. Pereira. (*Mat. Med.*, ii. 548.) A Swede, affected with general paralysis, was given one-eighth of a grain of strychnine three times a day for several weeks. The dose was then increased to one-quarter of a grain, and afterward to half a grain, with the same frequency, for many days, without any marked effect. But one morning the patient was found insensible, the face and chest of a deep purple color; the respiration had ceased, and the whole body was in a state of tetanic spasm and rigid. The symptoms passed off, and the man became apparently sensible; but another paroxysm soon occurred, and proved rapidly fatal.

In regard to the *diagnosis* of strychnine poisoning, the only disease with which its symptoms could be confounded is *tetanus* arising from ordinary causes. But there is rarely any difficulty in determining the true nature of the case. Thus, in poisoning the symptoms appear suddenly in a violent form; the muscles of the hands are the first, and those of the jaws the last, to become affected; there is usually a complete intermission in the symptoms; and they rapidly run their course, rarely lasting over a few hours at most. On the

other hand, in the disease the symptoms are slowly developed; the muscles of the jaws are the first, and those of the hands the last, to become involved; there is at most only a remission of the rigid state of the system; and death rarely occurs within twenty-four hours, the case often being protracted for several days. Dr. Hammond states that in ordinary tetanus, epigastric pain, due to spasm of the diaphragm, is an early and prominent symptom; whereas in strychnine poisoning this symptom is absent. (*Diseases of the Nervous System*, 555.) Pain in the epigastrium has, however, been present in strychnine poisoning; and also in several instances of poisoning by nux vomica.

Period when Fatal.—A case is recorded in which a young man, through the ignorance of a druggist, took one grain and two-thirds of strychnine, with the same quantity of nux vomica, and "he very soon afterward complained of some extraordinary sensations, and almost immediately expired." (*Amer. Jour. Med. Sci.*, April, 1854, 537.) In a case privately communicated to Dr. Taylor, ten grains of strychnine, given in mistake for sulphate of quinine, proved fatal in ten minutes. (*On Poisons*, 781.) In the case of Dr. Warner, already mentioned, death occurred in about eighteen minutes after the poison had been taken. Dr. Geoghegan, of Dublin, relates an instance in which five grains proved fatal in from twenty to twenty-five minutes; and in Dr. Barker's case, already cited, six grains caused death in about thirty minutes. In a case described by Dr. Theinhart, in which nearly thirty grains of the poison were taken, violent symptoms appeared in about fifteen minutes, and, after four convulsive paroxysms, death occurred in half an hour. (*Amer. Jour. Med. Sci.*, Jan. 1848, 303.) Dr. Gray mentions an instance in which death occurred in five minutes after the invasion of the symptoms.

On the other hand, in the well-known case of Cook, poisoned by Palmer, the symptoms were delayed for nearly an hour, and death occurred in about an hour and a quarter after the poison had been taken. We have elsewhere recorded a case in which a man named Freet took an unknown quantity of the poison, and violent symptoms appeared in about half an hour, but death did not take place until an hour later. (*Ohio Medical and Surgical Journal*, March, 1864, 95.) In a case described by Dr. Steiner,—that of Dr. Gardiner, of Washington City,—death did not occur until after the lapse of three hours and a half, although violent symptoms were present

shortly after the poison had been taken. (*Report on Strychnia*, Philadelphia, 1856.) A still more protracted case has been reported by Dr. Paley, in which death did not occur until after the lapse of about five hours. (*Med.-Chir. Rev.*, Oct. 1860, 382.) Dr. J. J. Reese, of Philadelphia, reports the case of a woman, in which death was delayed for from five to six hours. (*Amer. Jour. Med. Sci.*, Oct. 1861, 409.) At a subsequent trial of this case, as personally informed by Wm. H. Miller, Esq., who was engaged in the trial, it fully appeared in evidence that the deceased had taken from five to six grains of the poison, and death was delayed something over six hours.

The most protracted case in this respect yet reported is related by MM. Tardieu and Roussin (*Ann. d'Hyg.*, July, 1870, 128), in which an abandoned young woman survived the effects of a large dose of the poison for a period of about *eighteen hours* after the symptoms first appeared, the woman being intoxicated when first seen. On inspection, eleven grains (.71 gramme) of solid strychnine were found adherent to the mucous membrane of the stomach; about three grains of the absorbed poison were extracted from the tissues.

Fatal Quantity.—There seems to be much difference in the susceptibility of different persons to the action of strychnine. Dr. G. B. Wood mentions an instance in which a lady was thrown into violent and even alarming spasms, almost threatening suffocation, by one-twelfth of a grain of strychnine. (*Therapeutics*, i. 834.) In a case related by M. Duriau, one-sixth of a grain taken by a woman, aged twenty-eight years, produced in ten minutes afterward violent tetanic convulsions, in which the whole body became rigid; similar attacks ensued at intervals of a few minutes between each, and these were succeeded by a sense of burning in the epigastrium and pharynx, and great irritability of the stomach, which lasted for not less than six weeks. (*Amer. Jour. Med. Sci.*, Oct. 1862, 562.) In the case of Dr. Warner, it is believed that not over *half a grain* of sulphate of strychnine had been taken. This seems to be the smallest quantity that has yet proved fatal to an adult. In a case reported by Dr. Ogston, three-quarters of a grain destroyed the life of a man in three-quarters of an hour; and Dr. Watson relates an instance in which a similar quantity caused the death of a girl, aged twelve years, in about one hour. Mr. Bennett describes a case in which one grain and a half caused the death of a girl, aged thirteen years, in two hours and a half (*Lancet*, Aug. 1850, 462); and Mr. C. Bullock relates a case

(*Amer. Jour. Pharm.*, July, 1870, 309) in which a similar quantity proved fatal. Dr. Pereira (*Mat. Med.*, ii. 549) cites the instance of a lady who died in less than two hours from the effects of between two and three grains of the poison.

Recovery has not unfrequently taken place after comparatively large quantities of strychnine had been taken. A case of this kind in which five grains were taken, and another in which seven grains were taken in two doses of three and a half grains each at an interval of five hours, have already been cited. Wharton and Stillé quote three instances of recovery in each of which *four grains* of the poison had been swallowed (*Med. Jur.*, 624); and a fourth case of this kind is reported by Dr. Lescher, of Illinois, and still another by Dr. Waller (*Med. and Surg. Reporter,* Philadelphia, Oct. 1865, 277). In another instance, related by Dr. Givens, a young man swallowed, with suicidal intent, two large pills containing not less than ten or twelve grains of strychnine. Violent tetanic spasms soon ensued, and continued for five hours. In seven hours the spasms entirely subsided, leaving the patient quite prostrated, with much distention and tenderness of the epigastrium, and stricture and soreness of the throat, and of the muscular system in general. These effects gradually passed off, and in less than a week the patient was nearly well. Soon after the patient had taken the poison, vomiting occurred, but it is not certainly known that the pills were ejected. (*Med.-Chir. Rev.*, April, 1857, 502.)

In a case reported by Dr. Wilson (*Amer. Jour. Med. Sci.*, July, 1864, 70), a young man, twenty-two years of age, recovered in about fifteen hours, although it is believed that he had taken forty grains of strychnine. There is, however, in this instance much uncertainty as to the quantity of poison really taken; moreover, there seems to have been very early vomiting. In a case reported by Dr. Clark, a man laboring under *delirium tremens* swallowed over *twenty grains* of the poison, and eighteen hours afterward he was convalescent. (*Buffalo Med. and Surg. Jour.*, Nov. 1866, 135.) In this case, also, there was early vomiting. After the action of the emetics, the patient was kept under the influence of chloroform for eight consecutive hours, during which time all attempts to suspend its use were attended with a recurrence of the convulsions. In a more recent case, a young man, aged nineteen, voluntarily swallowed over *thirty grains* (two grammes) of crystallized strychnine at midnight

after a full meal. When first seen, at five o'clock the next morning, he was found in tetanic convulsions. Olive-oil, brandy, laudanum, and other remedies being employed, the patient was completely restored four days after taking the poison. (*New Remedies*, April, 1879, 117.) In a case recently reported by Dr. W. T. Parker, Assistant Surgeon U.S.A., a colored soldier, aged twenty-three years, fully recovered after having eaten, it is believed, about fifteen grains of solid strychnine. (*Medico-Legal Journal*, Dec. 1884, 375.)

Treatment.—This consists in the speedy administration of an emetic or the employment of the stomach-pump. As an emetic, finely-powdered mustard or zinc sulphate may be employed. The action of the emetic should be aided by the free use of warm demulcent drinks. On account of the difficulty of swallowing, or the rigid state of the jaws, it is sometimes impossible to resort to the use of emetics or the stomach-pump. Of the various remedies that have been proposed, the internal administration of *chloroform*, as first employed by Dr. Dresbach, of Tiffin, Ohio, seems to be much the most efficient. In a case in which a man had by mistake swallowed a solution of three grains of strychnine, and most violent symptoms were present in twenty minutes, Dr. Dresbach administered two drachms of chloroform, and there was complete relief in less than twenty minutes afterward. (*Amer. Jour. Med. Sci.*, April, 1850, 546.) In another instance, related by Dr. J. R. Smith, the inhalation of the vapor of chloroform was attended with similar results. (*Ibid.*, July, 1860, 278.) Another case of this kind, in which four grains of strychnine had been taken, is reported by Dr. Bly. (*New York Jour. of Med.*, Nov. 1859, 422.) So, also, in a case communicated to Dr. G. B. Wood, in which a robust young man had taken four grains of the poison and was seized with the most violent tetanic spasms, complete recovery took place under the use of chloroform, given both internally and by inhalation. (*U. S. Dispensatory*, 1865, 1357.) In this case it is stated that it was necessary to keep the patient under the influence of the chloroform for thirteen consecutive hours, during which two pounds were consumed by inhalation. Two drops were given every five minutes by the stomach, when the mouth could be opened. In a case related by Dr. G. W. Copeland, a man knowingly took five grains of strychnine, and was fully restored under the inhalation of chloroform continued for eleven hours. At no time in this instance was there vomiting, although twenty grains

of zinc sulphate had been given. (*Lancet and Observer*, Cincinnati, Jan. 1874, 41.)

As a chemical antidote, *tannic acid* has been strongly advised; and Dr. Kurzak, of Vienna, has performed a series of experiments upon inferior animals, from which it would appear that this substance, if administered early, has the property of suspending the action of the poison. He states that about twenty-five parts of tannin are required for one part of strychnine. In the absence of tannin in its pure form, a strong infusion of powdered gall-nuts or of green tea might be exhibited. (*North American Med.-Chir. Rev.*, July, 1860.) The utility of this acid is supposed to depend upon its uniting with the poison to form tannate of strychnine, which is insoluble in water, but readily soluble in acids. M. Bouchardat recommends, as an antidote, a solution of *iodine* in *potassium iodide*. The precipitate produced by this mixture is somewhat less soluble in diluted acids than that occasioned by tannic acid. It need hardly be remarked that neither of these substances should be relied on to the exclusion of emetics or the stomach-pump. Among the other substances that have been recommended as antidotes may be mentioned chlorine, bromine, animal charcoal, camphor, and lard, or fat. A case in which four grains of strychnine had been taken and recovery took place under the use of emetics and camphor, is related by Dr. Rochester. (*Buffalo Medical Journal*, March, 1856.)

Upon physiological grounds, Prof. Houghton was led to believe that strychnine and nicotine (the active principle of tobacco) might be mutually antidotal, and he cites a few experiments on frogs in support of this view. And Dr. O'Reilly, of St. Louis, has related an instance in which, acting upon this suggestion, he administered, in divided doses, an infusion of an ounce and a quarter of tobacco to a man who had taken six grains of strychnine, and the patient recovered. (*Med.-Chir. Review*, Oct. 1859, 387.) Since, however, in this instance, previous to the administration of the alleged antidote, an emetic had been given and operated, it is not certain that the recovery was in any way due to the effects of the tobacco. Another instance in which an infusion of tobacco was employed, and the patient recovered, has been reported by Dr. Chevers, of Calcutta. (*Ibid.*, Jan. 1867, 243.) But in this instance, also, there seems to have been vomiting prior to the administration of the tobacco; moreover, it appears that the patient, a girl aged

eleven years, had swallowed only a comparatively small quantity, perhaps very much less than one grain, of the poison.

For the purpose of testing the antidotal properties of nicotine, we administered to each of thirteen healthy cats half a grain of pure strychnine, the poison being passed in solution into the stomach by means of a stomach-tube. In some instances, as soon as symptoms of the poison appeared, an infusion of twenty grains of tobacco-leaves was administered, in the same manner as the poison; whilst in others, the tobacco-infusion was given along with the strychnine, the two solutions being thoroughly mixed. In some few cases the dose of tobacco was repeated. As the result of these experiments: one of the animals which had taken the mixed solutions immediately fell prostrate, breathed with difficulty, in three minutes voided urine, in eight minutes vomited a frothy mucus, and in ten minutes was able to run, with, however, a stiff gait; after an hour the animal appeared perfectly well, except a slight stiffness in walking. With this single exception, all the animals died, and in most instances within the usual period; one of them, however, that had taken the mixed solutions, manifested no symptom whatever for thirty-five minutes. In some instances the strychnine symptoms appeared to be not in the least affected by the tobacco; but in others they were of a compound nature. Several of the animals vomited. Before performing these experiments, it was ascertained that an infusion of twenty grains of tobacco, given alone, would produce serious symptoms; but in no instance, in six experiments, did it cause death.

From one hundred and forty-three experiments made by Dr. F. L. Haynes, upon rats, cats, rabbits, and dogs, with strychnine and tobacco or nicotine, he concluded that these substances were in no degree antagonistic. (*Proc. Amer. Philos. Soc.*, 1877, 596.)

M. Liebreich strongly advised *chloral* as antidotal to strychnine, and a number of instances are reported in which this substance was used with advantage. Dr. G. Gray reports a case in which twenty grains of strychnine had been taken, and under the administration of two drachms of chloral hydrate the patient entirely recovered. (*Amer. Jour. Pharm.*, Sept. 1880, 475.) More recently, Prof. V. Cervello has proposed, for this purpose, *paraldehyde*, he having found in a series of experiments that this agent completely antagonized enormous doses of strychnine. (*Medical News*, March, 1884,

361.) So, also, *amyl nitrite* has been advised as a physiological antidote.

Post-mortem Appearances.—The most constant appearances in death from strychnine are engorgement of the lungs, and fulness of the blood-vessels of the brain and its membranes, with a fluid condition and dark color of the blood. The heart is generally empty and flaccid. In some instances there is more or less redness of the mucous membrane of the stomach. Congestion of the liver, spleen, and kidneys has also been observed. The body usually presents a more or less livid appearance. One of the most striking characters in death from this substance is the rigid condition assumed by the body soon after death. In this state, the joints are fixed, the abdomen hard and tense, the legs extended, the feet arched, the fingers firmly closed, and the head thrown back. In a case reported by Dr. Paley, of Peterborough, death took place during a paroxysm, and the tetanic rigidity continued for some time afterward, the arms being crossed and forcibly bent over the chest, the hands rigidly closed, and the legs perfectly stiff; but in twenty-three hours there was no unusual rigidity about the limbs. (*Med.-Chir. Rev.*, Oct. 1860, 384.) In all the animals we have killed with this poison, the bodies were flaccid at the time of death, but they soon became rigid. A like result was observed by Prof. Ranke in seventeen dogs killed by strychnine: the time of the first appearance of rigidity varied from twenty-one to ninety-seven minutes after death. (*Ann. d'Hyg.*, April, 1881, 387.)

In the case reported by Dr. Theinhart, in which death took place in half an hour, the tongue, gums, and lips, as also the fingers and toes, were of a violet color; the fingers were closed, and the toes drawn in; and the whole body was as rigid as a stick of wood, and slightly bent upon itself. In a case in which a woman seems to have died almost instantaneously from the effects of strychnine, the inspection showed great rigidity of the muscles, the stomach contracted in the form of a dumb-bell, and the left heart most firmly contracted and empty, the right being also nearly empty. (*Med.-Chir. Rev.*, Oct. 1869, 552.) In Dr. Blumhardt's case, in which forty grains of strychnine had been taken and death occurred in an hour and a half, twenty-four hours after death the skin was found of a dark color, and the body excessively rigid. On opening the vertebral canal, a large quantity of thick fluid blood escaped. The plexuses

of the spinal veins and the pia mater were highly congested. The upper part of the spinal marrow was exceedingly soft, but the lower portion hard. The substance of the brain was slightly congested, but the membranes were healthy. The stomach was nearly normal, and contained a slimy mucus.

In the case of Freet, already mentioned, forty hours after death, the skin was livid, the body rigid, the hands clinched, and the toes drawn upwards. The lower extremities were stiff, but the arms relaxed. The pyloric end of the stomach was somewhat reddened; and the liver and lungs were gorged with dark liquid blood. The blood throughout the body was of a dark color and fluid. The brain was healthy, but its vessels were nearly destitute of blood. The kidneys and bladder were normal. In Dr. Steiner's case, eighteen hours after death, the body was extremely rigid, and the face, neck, and back were livid. The scalp and membranes of the brain were highly congested with dark liquid blood; but the substance of the brain and spinal marrow presented nothing abnormal. The heart was small, contracted, and contained no blood. The liver, spleen, and pancreas were natural, but the kidneys were highly congested. In the case described by Dr. Reese, six weeks after death, the body was found very rigid, and in a good state of preservation; the heart was healthy, and contained a considerable quantity of blood. In Dr. Paley's case, in which life was prolonged for about five hours, the only abnormal appearances found in the body, twenty-three hours after death, were slight traces of inflammation of the lining membranes of the stomach and ileum, and a generally congested state of the thoracic and abdominal organs; the heart was nearly empty, and the blood of a dark color and fluid.

The following case, in which a large quantity of the poison had been taken and proved rapidly fatal, is reported by Dr. Buck. (*Amer. Med. Times*, Oct. 1863, 205.) Four hours after death, the body was still warm, the face livid, eyes open, pupils natural, jaws firmly closed, lips slightly parted, and frothy matter was escaping from the mouth. The muscles of the neck were relaxed, the arms rigid, and the elbows fixed at right angles, with the forearms across the chest; the fingers were semi-flexed, and, when forcibly extended, would fly back; the same was true of the elbow. The legs were rigidly extended, the feet arched, and the great toes drawn in. In twenty-four hours after death, the neck, back, left arm, right shoulder, and

hip-joints were relaxed; but the other parts of the body were in the same condition as before. On opening the cranium, a large quantity of blood escaped from that cavity. The membranes of the brain were congested, but the brain and spinal marrow were healthy. The lungs, lining membrane of the trachea, and muscles in front of the neck were congested. The heart was firmly contracted, the ventricles empty, and only a very little blood in the auricles. The mucous membrane of the cardiac portion of the stomach was congested; all the other organs of the abdomen were healthy. A chemical examination of the contents of the stomach, by Dr. A. A. Hayes, of Boston, revealed the presence of a large quantity of strychnine.

Chemical Properties.

General Chemical Nature.—In its pure state, *strychnine* crystallizes in the form of colorless, transparent octahedra or in lengthened prisms. When precipitated from complex organic solutions, it often appears in the form of minute granules. As found in the shops, it is sometimes in the form of a white or dull-white amorphous powder, at other times in the form of well-defined crystals. Strychnine has a most intensely bitter taste, but it is destitute of odor. It is not decomposed either by the cold concentrated mineral acids or the caustic alkalies. When heated, it fuses to a brownish liquid, then undergoes decomposition, with the evolution of dense, white fumes; when heated in the flame of a spirit-lamp, it takes fire and burns with a yellowish smoky flame. If the heat be gradually increased, strychnine may be sublimed unchanged. According to Prof. Guy, it begins to vaporize at 174° C. (345° F.), and fuses at 221° C. (430° F.)

Strychnine has strong basic properties, and readily unites with acids to form *salts*, most of which are easily crystallizable. The salts of strychnine, except when containing a colored acid, are colorless; they have the intensely bitter taste of the pure alkaloid, and are equally poisonous. The *neutral sulphate*, $2C_{21}H_{22}N_2O_2 ; H_2SO_4$, crystallizes in the form of transparent, colorless, four-sided prisms, which are usually said to contain seven molecules of water of crystallization: later researches, however, indicate that the crystals contain sometimes five, and at other times six, molecules of water, but never seven, as assigned by Regnault. On exposure to the air, the crystals become

opaque from loss of water of crystallization. The *acid sulphate*, when crystallized, has the composition $C_{21}H_{22}N_2O_2,H_2SO_4,2H_2O$.

The *hydrochloride*, or *chloride*, $C_{21}H_{22}N_2O_2,HCl$, forms slender crystalline needles, which, according to Gerhardt, contain one molecule of water. The *nitrate* and the *acetate* appear in the form of beautiful silky needles; the latter of these salts, however, crystallizes with difficulty.

Solubility. 1. *In Water.*—When excess of pure powdered strychnine is digested at the ordinary temperature for twenty-four hours, with frequent agitation in distilled water, the solution then filtered, and the filtrate evaporated to dryness at a moderate temperature, it leaves a crystalline residue indicating that one part of the alkaloid had dissolved in 8333 parts of the liquid. It is usually stated that strychnine dissolves in 6667 parts of water at the ordinary temperature; but the above is the mean result of several very closely accordant experiments. Its solubility is much increased by a moderate heat, and much of the excess long remains in solution.

2. *In Ether.*—Excess of the finely-powdered alkaloid was digested at the ordinary temperature for twenty-four hours in *absolute* ether, and the mean of several experiments indicated that one part dissolved in about 1400 parts of the liquid. It is somewhat more soluble in ordinary ether. One part of the pure alkaloid dissolved in 1050 parts of commercial ether of specific gravity 0.733.

3. *Chloroform* readily takes up one part of the pure alkaloid in eight parts of the menstruum.

4. *Absolute alcohol*, when kept in contact at the ordinary temperature with excess of the alkaloid, with frequent agitation, for four hours, takes up one part in 207 parts of the liquid. Under similar conditions, one part of the alkaloid will dissolve in about 400 parts of common *whiskey*.

5. *Amyl alcohol*, when agitated for a few minutes with excess of the alkaloid at the ordinary temperature, dissolves one part in 122 parts of the menstruum.

6. *Benzene*, or *benzole*, of specific gravity 0.878, when frequently agitated for some hours with excess of finely-powdered strychnine, dissolved one part of the alkaloid in 140 parts of the fluid. On spontaneous evaporation, a benzene solution of strychnine leaves the alkaloid in the form of large, brilliant, octahedral crystals.

7. *Petroleum-ether*, of specific gravity 0.625, under like conditions,

dissolved only one part of strychnine in about 12,500 parts of the liquid.

From the foregoing facts, it is obvious that, other things being equal, strychnine is much more completely extracted from its aqueous solution or mixture by *chloroform* than by *ether;* however, the latter liquid will usually answer very well for the recovery of the poison. The use of chloroform for the extraction of the alkaloid from complex organic mixtures has been objected to, on the ground that it acts more solvently than ether upon foreign matters; but we have not found this objection to hold in ordinary practice. Strychnine is insoluble in the fixed caustic alkalies, and only very sparingly soluble in ammonia.

Most of the *salts* of strychnine are readily soluble in water and in alcohol, they being more freely soluble in the latter liquid than the pure alkaloid. They are also soluble to an appreciable extent in ether. Thus, we find that the acetate dissolves in about 10,000 times its weight of this liquid. The insoluble salts of the alkaloid are readily soluble in the presence of a free acid, even, with very few exceptions, of acetic acid.

Special Chemical Properties.—Concentrated *sulphuric acid* dissolves strychnine, as well as its colorless salts, to a colorless solution, which, upon the addition of a crystal of potassium dichromate, rapidly passes through a highly characteristic series of colors (see *post*, COLOR TEST). A crystal of potassium nitrate stirred in the sulphuric acid solution produces no visible change. Concentrated *nitric acid* dissolves the alkaloid and its salts without change of color, even upon the addition of stannous chloride: if the strychnine be contaminated with brucine, as is frequently the case as met with in commerce, it strikes a red or orange-red color with nitric acid. So, also, *hydrochloric acid* dissolves the pure alkaloid to a colorless solution. When moistened with a solution of potassium dichromate, strychnine acquires a beautiful golden-yellow color.

Pure *solutions* of strychnine, and of its salts, are colorless and odorless, and have the bitter taste of the pure alkaloid. Upon slow evaporation, they leave the poison in its crystalline form. An alcoholic solution of the free alkaloid quickly restores the blue color of reddened litmus-paper. This reaction is also perceptible in a saturated aqueous solution of the alkaloid.

The *taste* of strychnine, under certain conditions, is one of its

most characteristic properties, and it may be recognized even in highly diluted solutions. Thus, a single grain of a 1–50,000th pure aqueous solution of the alkaloid—equal to the 1–50,000th of a grain of strychnine—has a quite perceptible bitter taste. A similar quantity of a 1–100,000th solution has a perceptible taste, but this can hardly be said to be bitter. It has been asserted that even much less quantities of the poison than the last-mentioned may thus be indicated; but in our own personal experience we have not met with a person whose sense of taste extended beyond the quantities just stated. Moreover, the taste of these minute quantities is readily disguised by the presence of foreign substances. In a drop of a 1–10,000th solution the taste is usually very decided and well marked, even in the presence of a very notable quantity of foreign matter.

That the taste is equally or even more delicate for the detection of strychnine in its *pure state* than any of the known chemical tests, as has been asserted by some writers, is certainly erroneous. Nevertheless, this is one of the best corroborative tests yet known, and its application should never be omitted. On the other hand, it should be borne in mind that an *impure extract* from a complex mixture may have a bitter taste, due to the presence of strychnine, and yet fail to respond to the color-test for the alkaloid, the reaction being prevented by the presence of foreign matter. Should, under ordinary conditions, a bitter taste not be perceived, it would follow that at most there was only a very minute quantity of the alkaloid present. So, also, it must be remembered that other substances, such as quinine, quassia, colocynth, picrotoxin, and morphine, possess a somewhat similar bitterness. Of the bitter substances mentioned, quinine is the only one that, like strychnine, would be taken up to any notable extent by either chloroform or ether, when one or the other of these liquids was used for the extraction. The fluorescent properties of acid solutions of quinine readily distinguish it from strychnine.

In the following investigations in regard to the action of reagents upon *solutions* of strychnine, the alkaloid was employed in the form of a salt, but chiefly as the acetate. The fractions employed indicate the fractional part of a grain of the anhydrous alkaloid in solution in one grain of pure water. The results, unless otherwise indicated, refer to the behavior of *one grain* of the solution.

1. *The Caustic Alkalies.*

The fixed caustic alkalies and ammonia throw down from somewhat concentrated solutions of salts of strychnine a white, amorphous precipitate of the pure alkaloid, which in a little time assumes the crystalline form. From more dilute solutions the precipitate does not appear until after a little time, and it then separates in its crystalline state. Solutions still more dilute may entirely fail to yield a precipitate. The precipitate is insoluble in potassium and sodium hydrates, and only sparingly soluble in ammonia, but it immediately disappears upon the addition of almost any of the diluted acids. When a somewhat strong solution of a salt of the alkaloid is exposed to the *vapor* of ammonia, it immediately becomes covered with a white film, and in a little time changes to a nearly solid mass of crystals.

1. $\frac{1}{100}$ grain of strychnine, in one grain of water, yields, with either of the reagents, an immediate, copious precipitate, which very soon becomes converted into a mass of crystals of one or more of the forms illustrated in Plate X., fig. 1. If after the addition of the reagent the mixture be allowed to remain very quiet, it yields very beautiful compound stellate crystalline groups of the form illustrated in the lower part of the figure: these forms are especially apt to be produced if the alkaloid contains a little brucine.
2. $\frac{1}{1000}$ grain: after a few moments crystalline needles and groups begin to appear, and in a very little time there is a quite good deposit. If upon the addition of the reagent the mixture be stirred with a glass rod, it almost immediately yields a very good amorphous precipitate, which very soon changes into short crystalline needles.
3. $\frac{1}{2500}$ grain: after a few minutes a very satisfactory crystalline precipitate has formed. If the mixture be stirred, the formation of the precipitate is much facilitated, and it is more abundant.
4. $\frac{1}{5000}$ grain, when treated with a very small quantity of reagent, yields after some minutes, especially if the mixture be stirred, a very satisfactory crystalline precipitate.

The *alkali carbonates* produce, in solutions of salts of strychnine, reactions similar to those of the free alkalies.

It need hardly be remarked that the production of a white crystalline precipitate by either of the foregoing reagents is not in itself

positive proof of the presence of strychnine. The crystalline forms of this alkaloid, however, are somewhat peculiar. The true nature of the precipitate, even when present only in the most minute quantity, may be readily established by means of the test just to be mentioned.

2. *Color Test.*

This test, which is the most characteristic, and at the same time, when applied to the pure alkaloid, one of the most delicate yet known for the detection of strychnine, is based upon the development of a series of colors when a *sulphuric acid solution* of the alkaloid is treated with certain oxidizing agents. Marchand, in 1843, was the first to point out that when strychnine is dissolved in sulphuric acid containing a little nitric acid, and the mixture stirred with a small quantity of peroxide (dioxide) of lead, the liquid immediately acquires a deep blue color, which rapidly changes to purple or violet, then gradually to red, which very slowly fades.

This development of colors is due to the action of the nascent oxygen evolved by the acids and lead compound upon the strychnine. Any combination that will eliminate oxygen will produce these results, provided the substance from which it is evolved, or some substance evolved along with it from the oxidizing agent, does not interfere with the action of the nascent gas. Mack, in 1846, proposed the use of sulphuric acid and manganese dioxide, and about the same time Otto suggested this acid and potassium dichromate. More recently it has been proposed to substitute for these metallic combinations various other substances, such as potassium ferricyanide, chromic acid, the alkaline iodates, potassium permanganate, and ceric oxide. Most of these substances were advanced under the claim either that they were more delicate in their reaction or else less subject to interferences than those that had previously been proposed; but a careful and impartial comparative examination shows that at most there is but little difference between them in regard to delicacy of reaction, and that they are all about equally affected by the presence of certain foreign substances. Of these different oxidizing substances, we prefer, for this purpose, *potassium dichromate:* this salt is readily obtained in its pure crystalline state. For the detection of the very minute traces of the alkaloid, it is better to have the color-developing agent in the form of a minute crystal than in the state of powder. Manganese dioxide and lead dioxide dissolve

in sulphuric acid without change of color; but potassium dichromate, potassium ferricyanide, and ceric oxide impart a yellowish, while potassium permanganate gives a greenish color to the acid. These colors, however, at most undergo but slow change, and could not possibly be confounded with the series of colors produced by strychnine.

To apply this test, a small quantity of the alkaloid, or any of its salts, in the solid state, is placed on a piece of white porcelain or in a watch-glass over white paper, and dissolved in a drop of pure *concentrated sulphuric acid*, in which, if pure, it dissolves without change of color. A small crystal of potassium dichromate, or a small portion of either of the other color-developing agents, is now added to the solution, and, when moistened with the acid, slowly moved around in the liquid by means of a pointed glass rod, when, either immediately or in a few moments, the peculiar succession of colors, beginning with a beautiful blue, will manifest itself. The blue color quickly passes into purple, this into violet, and this more slowly into red, which very slowly fades. The liquid ultimately either acquires a yellow or a greenish color, or becomes entirely colorless; but these results are altogether independent of the action of the strychnine. An important point to be observed, when applying the test to a suspected substance, is the non-coloration by the acid alone.

As the intensity and duration of the colors thus produced depend very much upon the amount of strychnine operated upon, as well as the relative quantities of acid and color-developing agent employed, and the physical state of the latter, it is impossible to give any description that will fully meet every case; yet whenever developed they are so peculiar as to be readily recognized, even when only the merest trace of strychnine is present. With a very minute quantity of the alkaloid the blue color may continue only for a moment, or it may even be entirely absent, the mixture developing at first a purple or a violet color, quickly passing to red. To obtain the best results from these minute quantities, the acid should be very concentrated and added in very minute quantity, and only a very small fragment of the oxidizing agent employed.

Another method of applying the test is to place a small drop of sulphuric acid by the side of the strychnine, and then stir a very small crystal of potassium dichromate in the acid until it imparts a slight yellow color to the liquid, when the moistened crystal is

dragged over the strychnine, by means of a pointed glass rod; or, the colored acid may be allowed to flow over the alkaloid, by gently inclining the dish. For the recognition of minute quantities of the poison this method is even more delicate than that just described. Since, however, as we shall see hereafter, in examining a suspected deposit it is frequently important to know the action of the acid alone, this method is not always applicable. The test may also be applied to *solutions* of strychnine, by treating a drop of the liquid with a drop or two of concentrated sulphuric acid, and stirring in the cooled mixture a small quantity of the color-developing agent. This method, however, applies only to somewhat strong solutions of the alkaloid, and even under these circumstances the results are by no means as uniform as when the strychnine is in its solid state.

Delicacy of the test.—In the following examinations in regard to the limit of the reaction of this test, the quantities of strychnine were obtained by evaporating *one grain* of a corresponding solution of a salt of the alkaloid to dryness spontaneously. This method of evaporation is much preferable to that on a water-bath, since it much more frequently leaves the poison in its crystalline state, which is better adapted to the application of the test than the amorphous form. The results refer more especially to those produced by potassium dichromate as the oxidizing agent, and are based on very frequently repeated experiments.

1. $\frac{1}{100}$ grain of strychnine, in the form of acetate, when obtained in the manner just described, forms a very fine crystalline deposit, which, when examined by the test, yields a magnificent display of colors.
2. $\frac{1}{1000}$ grain leaves a quite good crystalline residue, which yields, with the test, results very similar to those under 1. The same quantity of the alkaloid in solution in one grain of water yields very satisfactory results.
3. $\frac{1}{10,000}$ grain: the residue consists of a number of well-defined crystals, which, when treated with the reagents, yield a perfectly satisfactory succession of colors. The results obtained from this quantity of the alkaloid, when free from foreign matter and manipulated with care, are just as satisfactory, so far as the evidence of the presence of the alkaloid is concerned, as those obtained from any larger quantity, the only difference being in the duration of the different colors.

4. $\frac{1}{500,000}$ grain: the residue usually contains a number of distinct microscopic crystals; when the deposit is moistened with a trace of the acid, and treated with a mere fragment of the potassium salt, it yields very satisfactory evidence of the presence of the alkaloid.
5. $\frac{1}{100,000}$ grain: if the residue is not much distributed, it usually contains some few minute crystals, and, when treated as under 4, yields a very distinct coloration. For the success of this reaction it is essential that the residue be deposited within a narrow compass, and that the merest trace of the acid and color-developing agent be employed. Under these circumstances it will yield quite satisfactory results. The acid is best applied by moistening the end of a small glass rod with the liquid and then drawing it over the deposit.

When collected at *one point*, and perfectly free from foreign matter, even a much smaller quantity of strychnine than the last-mentioned will yield, under the action of the test, a very distinct purplish or violet coloration, especially if the fragment of potassium dichromate be first moistened with the acid and then brought in contact with the strychnine. The residues obtained from solutions of the alkaloid may be collected within a small space, by allowing the liquid to evaporate in a very concave watch-glass; or, better still, as first advised by Messrs. Rodgers and Girdwood, by collecting the solution in a pipette provided with a small capillary point, and from this applying a minute drop of the liquid to a warmed surface, and repeating the operation, as the fluid evaporates, until a sufficient deposit is obtained.

The *limit* of this test, particularly when potassium dichromate is used as the color-developing agent, has been the subject of much misunderstanding. Thus, with this reagent in the hands of some experimentalists, the test failed with quantities of the alkaloid only a little less than the 1–2000th or 1–3000th of a grain. But that these failures were not due to any want of delicacy on the part of the method itself is quite apparent from the foregoing results. So, also, it has been claimed that some of the other oxidizing agents are more delicate in this respect than potassium dichromate; and, even, that free chromic acid is much more delicate than its potassium salt. Since, however, this salt, when properly applied, will produce a distinct coloration with the least quantity of strychnine visible to the

naked eye, and under the microscope with about the least crystal visible by this instrument, it is obvious that it reaches the possible practical limit of any of the color-developing agents.

It is not thus intended to imply that in regard to delicacy this method is superior to any yet proposed, but only that it is not inferior: similar results may be obtained at least by the employment of potassium ferricyanide, as first proposed by Dr. E. Davy, and potassium permanganate, as advised by Dr. Guy, and also manganese dioxide. It has been stated by some observers that the colors produced by powdered manganese dioxide and lead dioxide are much more intense than those produced by potassium dichromate; but this is true only of given quantities of the alkaloid, and depends upon the physical state of these metallic compounds, similar results being equally produced by finely-powdered potassium dichromate or potassium ferricyanide, as also by powdered potassium permanganate.

Interferences.—Although this test will serve to reveal the nature of the least visible quantity of strychnine when in its *pure* state, yet the presence of certain foreign substances may cause it to fail entirely, even when comparatively large quantities of the poison are present. In this respect the action of the different color-developing agents is about equally affected. Brieger, in 1850, first announced that the reaction was more or less interfered with by the presence of *morphine* and its salts, *quinine*, and *sugar* (*Chem. Gaz.*, viii. 408); and since then it has been asserted that *brucine*, *tartar emetic*, *nitric acid* and *nitrates*, *common salt*, *corrosive sublimate*, and various other substances, had a similar property. Many of these substances, however, even when present in relatively large quantity, exercise but little influence over the test; but others of them may entirely prevent its ordinary reaction.

Morphine belongs to the latter class of these substances. The influence of this substance is determined both by the *relative* and the *absolute* quantity present. Thus, when 1–100th of a grain *each* of strychnine and morphine, or of their salts, are thoroughly mixed by evaporating their mixed solutions to dryness, the residue yields, under the single action of the test, little or no indication of the presence of the strychnine, whereas a mixture consisting of 1–1000th of a grain each of the alkaloids yields very satisfactory evidence of the presence of that alkaloid. In other words, a very minute quantity of a mixture of *equal parts* of the alkaloids will yield much better results

than will be furnished by a larger quantity of the mixture. When the mixture contains *two* parts of morphine, as we have elsewhere shown (*Chem. News*, April, 1860, 243), the strychnine reaction may still be obtained, provided only a small quantity of the mixture be employed; but in the presence of *three* parts of morphine the reaction is no longer marked, even with a minute quantity of the mixture.

When these alkaloids exist in the same solution, they may be separated by rendering the mixture alkaline and agitating it with *chloroform*, in which the strychnine is very freely soluble, whilst the morphine is almost wholly insoluble, especially in the presence of a free alkali. It is therefore obvious that when strychnine has been extracted from organic mixtures by means of chloroform in the manner to be pointed out hereafter, this interference on the part of morphine to the color test does not exist. Experiments show that this is true, under certain conditions, of the chloroform extract obtained from a strongly alkaline mixture containing *one hundred parts of morphine* with only *one part of strychnine*, even when only 1–1000th grain of the latter alkaloid is present.

It is obvious, from what has been stated, that a given quantity of chloroform could extract from an alkaline mixture of strychnine and morphine only a very minute and limited trace of the morphine, whether only that trace or very many times that quantity of the alkaloid was present: hence, if that minute quantity (or more) of morphine was present with only a still less quantity of strychnine, the chloroform residue might then fail to respond to the color test for strychnine.

Since morphine is still less soluble in pure *ether* than in chloroform, this liquid may equally be employed for the separation of these alkaloids, especially if after the addition of the alkali the mixture be allowed to stand some minutes before being agitated with the liquid. It should be remembered, however, that strychnine is much less soluble in ether than in chloroform.

For the separation of strychnine and morphine, it has been proposed to precipitate the strychnine by a solution of potassium dichromate. But as this reagent also produces precipitates in strong solutions of salts of morphine, especially after standing some time, and, also, as the chromate of strychnine is but little less soluble in water than the pure alkaloid, it is obvious that we might have a

mixture of these alkaloids the precipitate from which would consist largely, or even entirely, of chromate of morphine; and, moreover, that even under the most favorable circumstances a given quantity of the strychnine would remain in solution, and thus entirely escape detection. In the presence of a free alkali potassium dichromate is converted, in part at least, into the monochromate, which is a more delicate precipitant of morphine than of strychnine.

Brucine, the alkaloid associated with strychnine in nux vomica, has the property even perhaps to a greater extent than morphine of disguising the color reaction of strychnine. Thus, a residue consisting of 1–100th grain each of strychnine and brucine fails to give, under the test, any indication of the strychnine; a mixture of 1–1000th grain each yields only a faint reaction; but a mixture of 1–10,000th grain each of the alkaloids yields very satisfactory evidence of the presence of strychnine. So, also, 1–10,000th grain of strychnine with 1–1000th grain of brucine yields little or no coloration; but 1–100th grain of strychnine with 1–1000th grain of brucine yields a very marked reaction, although somewhat masked. This interference on the part of brucine applies equally whether potassium dichromate, potassium ferricyanide, or manganese dioxide be employed as the oxidizing agent.

Although commercial strychnine generally contains more or less brucine, the latter is perhaps never present in sufficient proportion to interfere seriously with the color test for strychnine. These alkaloids may, at least for the most part, be separated, if not in only minute quantity, by treating a strong aqueous solution of their sulphates or acetates with very decided *excess* of ammonia, when the strychnine will be precipitated, whilst the brucine will remain in solution. Or, the alkaloids may be dissolved in hot absolute alcohol, which on cooling will deposit the strychnine, the brucine remaining in solution. Messrs. Dunstan and Short have recently advised a method, based upon the difference in the solubility of the ferrocyanide of strychnine and brucine, for the separation of the two alkaloids. (*Amer. Jour. Pharm.*, Nov. 1883, 579.) This method, however, applies only when comparatively large quantities of the alkaloids are present.

Nitrates, such as potassium nitrate, interfere with the normal reaction of the test to nearly or about the same extent as morphine; and the interference applies equally to the different color-developing

agents. In regard to the influence of *tartar emetic*, our own observations fully confirm those of Mr. Hagen (*Chem. Gaz.*, 1857, 397), namely, that this substance may be present even in very large excess without exerting any very marked influence; yet, when the mixture contains twenty or thirty parts of the compound, it may entirely disguise the ordinary reaction of the test. These observations are equally applicable in regard to the modifying influence of *sugar*. Since the nitrates, tartar emetic, and sugar are insoluble in chloroform and in ether, neither of these substances could be present with strychnine when the alkaloid is extracted from organic mixtures by either of these liquids.

A much more serious interference to this test than any yet mentioned is the presence of certain undefined *organic substances* frequently extracted from complex mixtures by chloroform and by ether. It is no unusual occurrence thus to obtain extracts which fail to reveal the presence of strychnine, even when comparatively large quantities of the alkaloid are purposely added. In fact, this is so frequently the case when only a very minute quantity of the poison is present, that, should a suspected extract fail to indicate the presence of strychnine, before concluding that the latter is entirely absent it may be best to add to a separate portion of the extract a very minute quantity of the pure alkaloid and determine whether the failure might not be due to this cause. The method for separating substances of this kind will be considered hereafter.

Fallacies.—It has been objected to this test that under its action various other substances, as *aniline*, *curarine*, *cod-liver oil*, *pyroxanthine*, *papaverine*, *narceine*, *veratrine*, and *solanine*, yield colors somewhat similar to or even identical with those produced from strychnine. When, however, the test is properly applied and observed, these objections have little or no practical force. Thus, all these substances, except aniline, unlike strychnine, yield their colors, or at least are colored, by sulphuric acid *alone;* and, furthermore, none of them, except curarine and cod-liver oil, even by the conjoined action of the acid and color-developing agent, yields, like strychnine, a series or quick succession of colors.

Should, however, *potassium permanganate* be employed as the oxidizing agent, a more or less blue or violet coloration may be developed, in the absence of strychnine, by various other organic substances besides those just mentioned. According to W. T. Sedgwick

(*Amer. Chem. Jour.*, Dec. 1879, 369), even bits of filter-paper, woody fibre, and shreds of cloth may produce under this reagent colors closely resembling those produced by strychnine. From an infusion of *Eupatorium perfoliatum* (boneset) this observer obtained, under the action of the permanganate, a magnificent bluish-purple color, whilst potassium dichromate and manganese dioxide produced no blue coloration whatever. The general chemical nature of some of the foregoing fallacious substances may now be briefly considered.

Aniline, in its pure state, is a colorless *liquid*, having a rather pleasant odor, and a sharp, acrid taste: it is obtained from coal-tar, and by the action of potassium hydrate upon indigo; it may also be obtained by various other methods. When treated with concentrated sulphuric acid, it undergoes no change of color, but throws down, if present in notable quantity, a white precipitate of aniline sulphate. The *salts* of this base are colorless, nearly tasteless, and, for the most part, readily crystallizable. The sulphate has been employed as a therapeutic agent. Pure aniline is readily soluble in chloroform, but its salts are almost wholly insoluble in this liquid.

When the *salts of aniline* are treated with concentrated sulphuric acid, they, like the salts of strychnine, yield no coloration; but when a crystal of potassium dichromate, or a small portion of any of the other oxidizing agents, is stirred in the acid mixture, the latter slowly acquires a yellowish or greenish tint, then presents bluish streaks, and after a little time assumes a beautiful deep blue color, which undergoes little or no change for half an hour or even much longer, but finally becomes nearly or entirely black. It is thus obvious that the reaction of this substance bears but little similarity to that of strychnine, about the only resemblance being in the production of a deep blue color. But in the case of strychnine, as remarked by Dr. Guy, this color is the first produced, and is developed either immediately or at most within a few moments, and is quickly followed by other characteristic colors, it being itself exceedingly transient; whereas in the case of aniline this color is but slowly developed, is preceded by other colors, and when once established is exceedingly persistent, and ultimately becomes black. Dr. Letheby reports (*Chem. News*, v. 71) two cases of accidental poisoning by nitro-benzole, in which he found that it was changed in the animal body into aniline.

Curarine is the name applied to the active principle, or alkaloid,

found in Woorara, or Curara, the substance employed by the Indians of South America for poisoning their arrows. Much doubt exists as to the true nature of woorara. According to Waterton, it is prepared from several different plants, two species of poisonous ants, and the fangs of certain snakes; while Schomburgk states that it consists of vegetable matter alone, and chiefly of an extract of the bark of the *Strychnos toxifera*, a tree found native in Guiana. Various other statements have been made in regard to its composition. That there are at least several varieties of this substance current among the different tribes of Indians seems to be fully established by the investigations of Drs. Hammond and Mitchell (*Amer. Jour. Med. Sci.*, July, 1859, 13–61); and it is even probable that each tribe has its own method for preparing the poison. It was formerly believed that the poisonous properties of woorara were due to the presence of strychnine; but this alkaloid has not been found in any of the specimens yet examined. In fact, the physiological effects of this substance are the very opposite to those of strychnine, and it has even been advised as an antidote in poisoning by that alkaloid.

Woorara is usually described as a hard, black or nearly black, brittle, resin-like solid, of an intensely bitter taste; in the state of powder it has a dark brown color. It is, for the most part, readily soluble in water and in alcohol, but is only very slightly acted upon by *ether* and *chloroform*, even in the presence of a free alkali. The statements in regard to the chemical properties of this substance have been somewhat conflicting. The active principle, or curarine, as obtained by MM. Roulin and Boussingault, who were the first to isolate the alkaloid, was in the form of a transparent solid, having a pale yellow color and an exceedingly bitter taste. It, as well as all its salts, was uncrystallizable. According to Bernard, curarine dissolves in concentrated sulphuric acid with the production of a beautiful carmine color; and Pelikan states that under the combined action of this acid and a color-developing agent, as potassium dichromate or a current of electricity, it yields a brilliant red color. It would appear that M. Preyer obtained curarine, as well as its soluble salts, in the crystalline form. (*Chem. News*, London, July, 1865, 10.) According to this observer, the pure alkaloid yields with concentrated sulphuric acid a magnificent and lasting blue color; while with this acid and potassium dichromate it yields much the same series of colors as strychnine. With strong nitric acid it yields a purple coloration.

A specimen of ordinary woorara, kindly furnished us in liberal quantity by Dr. S. Weir Mitchell, has the following properties, its physical appearances being the same as those just described. When treated in its crude state, with concentrated *sulphuric acid*, it slowly yields, without entirely dissolving, a reddish-brown solution, which, when stirred with a small portion of potassium dichromate, or any other oxidizing agent, gives a series of colors very similar to that produced from a very impure mixture of strychnine. Concentrated *nitric acid* dissolves it, with evolution of nitrous fumes, to a deep reddish-brown solution. It is for the most part readily soluble in water, especially upon the application of heat; the insoluble portion consists apparently of vegetable fragments. The filtered aqueous solution has a deep brownish color, an intensely bitter taste, and a just perceptible acid reaction. It is about equally soluble in strong alcohol. The concentrated aqueous solution yields with a solution of potassium dichromate a yellow, amorphous precipitate, which, when washed and treated with a small quantity of concentrated sulphuric acid, yields a series of colors not to be distinguished from that produced under similar circumstances from the chromate of strychnine. This precipitate, however, differs from the strychnine compound in being uncrystallizable, and rather readily soluble in water.

When a strong aqueous solution of several grains of an alcoholic extract of the crude poison is rendered strongly alkaline with potassium hydrate and agitated with *chloroform*, this liquid remains colorless, and leaves, upon spontaneous evaporation, a slight, yellowish, gum-like residue, having an intensely bitter taste. When a minute portion of this residue is touched with a drop of *sulphuric acid*, it acquires a red color, and very soon dissolves to a solution of the same hue; if a small crystal of potassium dichromate be now stirred in the solution, it produces a series of colors the perfect counterpart of that from strychnine, with perhaps the exception that the blue and purple colors are somewhat more persistent than those from an equal quantity of the latter substance. Under the action of *nitric acid*, the chloroform residue assumes a red color, and dissolves to a reddish solution; this color is discharged by heat, and the cooled liquid remains unchanged on the addition of stannous chloride. The alkaline solution from which the chloroform extract was obtained has an intensely bitter taste, and yields with a solution of potassium

dichromate a rather copious amorphous precipitate, having the same properties as the precipitate from an aqueous solution of the crude poison. When a small quantity of the alkaline solution is treated with sulphuric acid, it acquires a beautiful purple color, which on the addition of a crystal of potassium dichromate is changed to a deep blue, followed by purple and the other characteristic colors. The alkaline solution also yields other reactions, indicating that but little of the active principle had been removed by the chloroform. Various efforts were made to obtain this principle, and some of its compounds, in the crystalline state, but in all cases without success.

It thus appears that this sample of woorara contains a principle having certain chemical properties in common with strychnine. Thus, like strychnine, it has an intensely bitter taste; yields under the combined action of sulphuric acid and an oxidizing agent a particular series of colors; and its potassium dichromate precipitate yields, with this acid alone, similar results. But these are about the only respects in which it resembles that alkaloid. Among the differences existing between this principle, at least in the sample under consideration, and strychnine, may be mentioned the following: it and all its compounds are *uncrystallizable;* it is colored by sulphuric acid *alone;* its potassium dichromate precipitate is rather readily *soluble* in water, and is amorphous; it is almost wholly *insoluble* in chloroform, and readily soluble in potassium hydrate; and its solutions are *not* precipitated by the caustic alkalies.

Three grains of the above woorara administered in solution to a young cat produced no appreciable effect whatever; although the animal was closely watched for twelve hours. But a very small quantity of the paste introduced under the skin of the inside of the thigh of a similar animal produced almost immediate stupor, and in eight minutes complete prostration; this condition continued, with occasional convulsive movements, for some hours, after which the animal completely recovered.

Cod-liver oil has also been mentioned as a source of fallacy. This substance when treated with sulphuric acid *alone* yields a series of colors which might be confounded with that produced from strychnine by the combined action of this acid and an oxidizing agent. But as strychnine yields no coloration with sulphuric acid alone, it is obvious that when the acid is applied first and its action observed, all grounds for objection, so far as this oil is concerned, are at once

removed. Moreover, the physical state of cod-liver oil would at once distinguish it from strychnine, or any of its salts, in the solid state.

The objections in regard to the other substances heretofore mentioned have already been answered, namely, that they are colored by sulphuric acid alone, and under no circumstance do they yield a quick succession of colors. Thus, *pyroxanthine*, which has a bright *red color*, yields with the acid a blue solution; *papaverine*, a purple; *narceine*, a reddish-yellow or brownish; *veratrine*, a yellow, slowly becoming crimson; and *solanine*, an orange-brown mixture. It may be remarked that the exact tint of color produced by the acid with at least some of these substances is more or less modified by the quantity of material employed.

In addition to the substances now considered, there are a number of alkaloids and other organic proximate principles which, when treated either with sulphuric acid alone or with this acid and potassium dichromate, give rise to more or less coloration. The action of this test with a number of these substances was first examined by M. Eboli (*Chem. Gazette*, 1856, 251); then by Dr. T. E. Jenkins, of Louisville, Ky., who extended the investigation to about fifty of these principles (*Semi-Monthly Med. News*, April, 1859, 214); and still more recently by Dr. Guy, of London (*Chemical News*, Aug. 1861, 113), who added some sixteen substances to those examined by Dr. Jenkins. But of all the substances thus and since examined, exclusive of some already mentioned, none gave results resembling the reactions of strychnine, even to the extent of those already considered.

Galvanic Test.—This in principle is the same as the preceding method, only that the oxygen is rendered nascent by a current of voltaic electricity, instead of being evolved from a metallic oxide, by means of sulphuric acid. It may be applied, according to Dr. Letheby, who, we believe, first advised the process (*Lancet*, June, 1856, 708), by placing a drop of the strychnine solution in a cup-shaped depression made in a piece of platinum-foil, evaporating the liquid at a low temperature, and moistening the residue with a small drop of concentrated sulphuric acid. The foil is then connected with the platinum pole of a single cell of Grove's or Smee's battery, and the acid liquid touched with the platinum terminal of the negative pole. In a moment the violet coloration manifests itself in great intensity.

In regard to the delicacy of this method, it is much the same as that of the test as ordinarily applied. Thus, according to our own experiments, the 1–10,000th of a grain of strychnine yields a fine display of colors; and the 1–100,000th of a grain, a distinct reaction. Since, however, this process is not so readily applied, and is about equally open to the interferences and so-called fallacies that hold against the ordinary method, it seems to possess no advantage over the latter. In fact, for the detection of very minute traces of strychnine it is less satisfactory than the ordinary method.

3. *Potassium Sulphocyanide.*

This reagent throws down from solutions of salts of strychnine, when not too dilute, a white crystalline precipitate of strychnine sulphocyanide, which, according to Nicholson and Abel, has the composition $C_{21}H_{22}N_2O_2,HCyS$. The precipitate is insoluble in excess of the precipitant, and but sparingly soluble in diluted acetic and hydrochloric acids.

1. $\frac{1}{100}$ grain of strychnine, in one grain of water, yields an immediate crystalline deposit, and in a few moments the mixture becomes a nearly solid mass of crystals, of the forms shown in Plate X., fig. 2.
2. $\frac{1}{1000}$ grain: on stirring the mixture, in a very little time it throws down crystals, and soon there is a very satisfactory deposit.
3. $\frac{1}{5000}$ grain yields, especially if the mixture be stirred, after some minutes, a satisfactory deposit of crystalline needles.

Potassium sulphocyanide also produces white crystalline precipitates in solutions of several other alkaloids.

4. *Potassium Iodide.*

Somewhat strong solutions of salts of strychnine yield with potassium iodide a white crystalline precipitate, which is insoluble in excess of the precipitant and in the free alkalies, and only slowly soluble in large excess of acetic, nitric, and hydrochloric acids. The formation of the precipitate is much facilitated by stirring the mixture with a glass rod.

1. $\frac{1}{100}$ grain of strychnine: in a few moments the mixture becomes a nearly solid mass of crystals, of the same forms as those produced by the preceding reagent (Plate X., fig. 2).

2. $\frac{1}{1000}$ grain: after a few minutes, especially if the mixture be stirred, a quite good deposit of stellate groups of crystals.
3. $\frac{1}{5000}$ grain: after several minutes there is a quite satisfactory crystalline deposit.

The precipitates produced by this and the preceding reagent cannot readily be confirmed by the color test.

5. *Potassium Dichromate.*

This reagent produces in solutions of salts of strychnine a bright yellow precipitate of strychnine chromate, which almost immediately becomes crystalline. The precipitate is insoluble in excess of the precipitant, and in acetic acid, and only very sparingly soluble in diluted nitric acid, but readily soluble in the concentrated acid. The fixed caustic alkalies slowly decompose the precipitate, with the elimination of pure strychnine, which, unless from dilute solutions, assumes the crystalline form, and may be extracted by chloroform. This liquid will also extract portions of the pure alkaloid from aqueous mixtures of the chromate, without dissolving a trace of the latter. From dilute solutions of strychnine the reagent produces no immediate precipitate, but the latter separates after a time in the crystalline form; under these circumstances the formation of the precipitate is much facilitated by stirring the mixture with a glass rod.

1. $\frac{1}{100}$ grain of strychnine yields a very copious precipitate, which in a very little time becomes a dense mass of bush-like crystals.
2. $\frac{1}{500}$ grain: an immediate deposit, and very soon a copious, crystalline precipitate. If after the addition of the reagent the mixture be allowed to remain quiet, the precipitate, after a little time, forms beautiful dendroidal groups of crystals, Plate X., fig. 3.
3. $\frac{1}{1000}$ grain yields no immediate precipitate, but very soon crystals appear, and in a few minutes there is a quite good deposit. If the mixture be stirred, it quickly yields a very good crystalline precipitate.
4. $\frac{1}{2500}$ grain: on stirring the mixture for a few moments it yields streaks of granules along the path of the glass rod, and soon a quite good deposit of octahedral and bush-like crystals, Plate X., fig. 4.
5. $\frac{1}{5000}$ grain: if the mixture be stirred, after some minutes a very

satisfactory deposit of small octahedral crystals and plates appear.

6. $\frac{1}{10,000}$ grain: when treated with a small quantity of reagent and the mixture stirred, it yields, after several minutes, small granules; after about twenty minutes there is a very satisfactory microscopic crystalline deposit of long plates, granules, and small octahedral crystals.

If the supernatant liquid be decanted from any of the above deposits, and the dried crystals touched with a small drop of concentrated *sulphuric acid,* they immediately assume a magnificent blue color, quickly changing to purple or violet, and dissolve to a purple or violet solution, which, passing through various shades, becomes red, then slowly fades in color. In other words, these crystals may be confirmed by the *color test* by the simple addition of sulphuric acid. The precipitate obtained from the 1–10,000th of a grain of strychnine, in solution in one grain of water, will, in this manner, yield a magnificent display of colors; and even the least microscopic crystal of the compound, when touched under this instrument with a very minute drop of the acid, will yield a very distinct coloration. It must, however, be borne in mind that a solution of strychnine may be too dilute to yield any precipitate whatever with this reagent, and yet have a distinctly bitter taste, and leave upon spontaneous evaporation, even of a single drop of the solution, a residue, which when examined by the color test in the ordinary manner, will yield very satisfactory results. Statements have been made in regard to the delicacy of this test which are well calculated to lead to erroneous conclusions.

For the separation of the precipitate, for the application of this confirmatory reaction, from dilute solutions of the alkaloid, it is best to stir the mixture, by means of a glass rod, in a watch-glass, and then allow it to repose for about half an hour, when the crystallized deposit will be found strongly adherent to the glass, and thus permit the ready separation of the supernatant liquid by decantation. Or, the mixture may be allowed to evaporate spontaneously to dryness, and the residue touched with a drop of pure water, which will readily dissolve any excess of the reagent present, while the attached crystals of the strychnine compound will remain.

As potassium dichromate also produces yellow crystalline precipitates with *brucine, narceine, codeine,* and some few other principles,

and amorphous deposits with *morphine*, *narcotine*, and a number of other substances, it is obvious that the mere production of even a crystalline precipitate by this reagent is not in itself positive evidence of the presence of strychnine. However, the crystalline form of the strychnine compound as usually produced is somewhat peculiar; and when the crystals yield a positive reaction with sulphuric acid, the results are perfectly unequivocal. Even a positive reaction by this acid from an amorphous deposit would exclude every other known substance, except the active principle of certain kinds of the woorara poison. By this method, therefore, the two most characteristic tests yet known for the recognition of strychnine may be applied to the same quantity of the poison.

Chromate of Strychnine which had been preserved for some years, when touched with sulphuric acid failed to yield satisfactory colorations; but on the addition of a mineral alkali and extraction with chloroform, the alkaloid was recovered unchanged.

Potassium Monochromate occasions no precipitate in neutral solutions of salts of strychnine, unless they be very concentrated. But with acidulated solutions—provided they do not contain very large excess of a mineral acid—it produces results similar to those by the dichromate, due to the fact that the free acid converts the reagent, in part at least, into the latter salt. One grain of a 1–100th neutral solution of the alkaloid yields, especially after a little time, a quite good crystalline deposit, very similar to that produced by potassium sulphocyanide (Plate X., fig. 2). This, however, is very nearly the limit of the reaction of the reagent under these conditions.

6. *Auric Chloride.*

Trichloride of gold produces in solutions of salts of strychnine, even when highly dilute, a yellowish, amorphous precipitate, which after a time becomes more or less crystalline. The precipitate is insoluble in acetic acid, and only sparingly soluble in diluted nitric acid; when treated with potassium hydrate, it slowly assumes a dark color.

1. $\frac{1}{100}$ grain of strychnine, in one grain of water, yields a very copious deposit, which at first has an orange-yellow color, but soon becomes yellow and more or less crystalline, forming groups of bush-like crystals and granules. If the precipitate contains even but little foreign matter, it may remain amorphous.

2. $\frac{1}{1000}$ grain: a copious, yellow precipitate, which in a little time becomes converted into groups of crystals, Plate X., fig. 5.
3. $\frac{1}{10,000}$ grain: a very satisfactory, yellowish deposit, which soon yields small crystalline groups.
4. $\frac{1}{25,000}$ grain: a very satisfactory turbidity.
5. $\frac{1}{50,000}$ grain yields a very distinct cloudiness.

When the precipitate from *ten grains* of a 1–5000th or more dilute solution of the alkaloid is boiled in the mixture, the deposit dissolves to a clear yellow solution, and it is redeposited with little or no change as the liquid cools; the precipitates from stronger solutions, when treated in this manner, do not entirely dissolve, but undergo more or less decomposition, with the deposition of metallic gold upon the sides of the tube. Potassium hydrate dissolves the precipitate from a 1–5000th solution to a clear liquid; but the deposit from stronger solutions is not readily soluble in this mineral alkali. Upon the application of heat, the potassium solution acquires a purplish color and throws down a precipitate.

Auric chloride also produces yellow precipitates with many other substances, but the crystalline form of the strychnine deposit is somewhat peculiar. The formation of these crystals, however, as already intimated, is readily interfered with by the presence of foreign matter.

The true nature of the strychnine precipitate, when in not too minute quantity, may be established by gently evaporating the mixture to dryness, treating the residue with a small drop of sulphuric acid, and then stirring in the mixture a minute crystal of potassium dichromate, when the strychnine series of colors will be developed. The residue from 1–100th grain of strychnine will in this manner readily yield satisfactory results; but 1–1000th grain yields little or no coloration. This reaction is much interfered with by the presence of large excess of the gold reagent.

7. *Platinic Chloride.*

This reagent produces in solutions of salts of strychnine a pale yellow, amorphous precipitate of strychnine chloroplatinate, $2C_{21}H_{22}N_2O_2,HCl;PtCl_4$, which soon becomes crystalline. The precipitate, especially when it has assumed the crystalline form, is insoluble in acetic and diluted nitric acids: it is unchanged in color and only sparingly soluble in the caustic alkalies.

1. $\frac{1}{100}$ grain of strychnine yields a very copious precipitate, which soon becomes a mass of crystals.
2. $\frac{1}{1000}$ grain: a very good deposit, which is soon converted into beautiful crystals, Plate X., fig. 6.
3. $\frac{1}{5000}$ grain: on stirring the mixture it yields after a few moments a granular deposit, and after a few minutes a quite good crystalline precipitate.
4. $\frac{1}{10,000}$ grain yields after a little time, if the mixture has been stirred, a quite satisfactory deposit of stellate groups of crystals and granules.

This reagent also produces yellow crystalline precipitates with nicotine, potassium compounds, and ammonia; a granular deposit with morphine; and amorphous precipitates with a number of substances; but the strychnine precipitate is usually readily distinguished from these by its crystalline form. In mixtures containing much foreign organic matter, however, the strychnine compound may not assume the crystalline state.

Palladium Chloride throws down from solutions of salts of strychnine a yellow precipitate, which assumes the same crystalline form as that produced by the platinum reagent; the limit of the reaction is also the same.

8. *Picric Acid.*

An alcoholic solution of this acid occasions in solutions of salts of strychnine a yellow precipitate of strychnine picrate, which is only sparingly soluble in large excess of acetic acid and in alcohol. The precipitate is readily soluble, to a colorless solution, in sulphuric acid, and the mixture, when treated with a color-developing agent, yields the peculiar strychnine-series of colors; not, however, in the same intensity as many of the other salts of the alkaloid.

1. $\frac{1}{100}$ grain of strychnine yields a very copious, amorphous precipitate, which slowly becomes converted into a mass of irregular crystalline tufts.
2. $\frac{1}{1000}$ grain: a very good precipitate, which soon becomes changed into crystals, having the very singular forms illustrated in Plate XI., fig. 1.
3. $\frac{1}{10,000}$ grain: on stirring the mixture it yields, after a little time, a very satisfactory granular deposit.
4. $\frac{1}{25,000}$ grain yields after a little time, if the mixture has been stirred, a quite perceptible granular precipitate.

Picric acid also produces crystalline precipitates with various other substances. The crystalline form, however, of the strychnine compound is somewhat peculiar.

9. *Corrosive Sublimate.*

Mercuric chloride throws down from strong neutral solutions of salts of strychnine a white, amorphous precipitate of the double chloride of strychnine and mercury which is readily soluble in acids, even acetic acid. After a time the precipitate becomes crystalline.

1. $\frac{1}{100}$ grain of strychnine yields a very copious precipitate, which in a little time becomes somewhat granular, then changes into groups of radiating crystals, usually attached to a granular nucleus, and aggregations of large granules, Plate XI., fig. 2. The general form of these crystals is readily modified by slight circumstances.
2. $\frac{1}{500}$ grain: after some minutes the mixture yields a quite satisfactory precipitate of stellate crystals.

In solutions but little more dilute than the last-mentioned, the reagent fails to produce a precipitate, even after long repose.

10. *Potassium Iodohydrargyrate.*

This reagent may be prepared by dissolving one part of pure corrosive sublimate in one hundred parts of water and then adding just sufficient potassium iodide to redissolve the scarlet precipitate first produced, which will require very nearly four parts of the iodine compound. A small quantity of this mixture throws down from solutions of salts of strychnine a dull white precipitate of the double iodide of strychnine and mercury, which is insoluble in excess of the precipitant and in the caustic alkalies, as well as in acetic and hydrochloric acids. The precipitate is also insoluble in alcohol; concentrated sulphuric acid readily decomposes it, with the production of a reddish-brown or purplish color.

1. $\frac{1}{100}$ grain of strychnine, in one grain of water, yields a very copious curdy precipitate, which after a little time becomes partly converted into granules and short, crystalline needles. If the reagent contain an excess of potassium iodide, the precipitate assumes the same crystalline form as when this salt alone is employed as the precipitant.
2. $\frac{1}{1000}$ grain yields a rather copious precipitate.

3. $\frac{1}{10,000}$ grain: a quite good precipitate, which in a little time becomes converted into opaque granules and short, irregular needles. On the addition of a few drops of acetic or hydrochloric acid, the precipitate is soon changed into irregular groups of rather long needles.
4. $\frac{1}{50,000}$ grain yields a quite distinct precipitate, and in a little time a very satisfactory deposit. This deposit is very similar in appearance to that produced from dilute solutions of atropine by bromohydric acid, as illustrated in Plate XII., fig. 6.
5. $\frac{1}{100,000}$ grain: no immediate change, but in a very little time the mixture becomes cloudy, and soon yields a very satisfactory deposit of opaque granules and short, irregular needles.

The production of a white precipitate by this reagent is common to solutions of most, if not all, of the alkaloids.

11. *Potassium Ferricyanide.*

This reagent produces in quite strong neutral solutions of salts of strychnine a yellowish, amorphous precipitate, which in a little time becomes crystalline. The precipitate is only slowly soluble in acetic acid, but readily soluble in the stronger acids, and is, therefore, not produced in their presence.

1. $\frac{1}{100}$ grain of strychnine yields a quite copious precipitate, which in a few moments becomes converted into a mass of beautiful groups of crystals, Plate XI., fig. 3.
2. $\frac{1}{500}$ grain: a very good crystalline precipitate.
3. $\frac{1}{1000}$ grain yields little or no indication of the presence of the strychnine, even after the mixture has stood half an hour or longer.

When a small portion of the precipitate, occasioned by this reagent, is treated with a drop of concentrated sulphuric acid, it, like that produced by potassium dichromate, dissolves with the production of the same series of colors as obtained by the color test as ordinarily applied. The least visible crystal of the deposit will respond to this reaction. It will be observed, however, that as a precipitant for strychnine, potassium ferricyanide in point of delicacy is far inferior to potassium dichromate.

Sodium Nitroprusside throws down from neutral solutions of salts of strychnine a white or dirty-white precipitate, which assumes the same crystalline form as that produced by potassium ferricyanide,

and the limit of the reaction is about the same. But, notwithstanding the contrary has been asserted, this precipitate, unlike that occasioned by potassium ferricyanide, dissolves without change of color in concentrated sulphuric acid.

Potassium Ferrocyanide fails to precipitate solutions of salts of strychnine, unless very concentrated and perfectly neutral. One grain of a 1–100th solution of the alkaloid will yield a quite good crystalline deposit; but this is very nearly the limit of the reaction.

12. *Iodine in Potassium Iodide.*

An aqueous solution of iodine in potassium iodide produces in solutions of salts of strychnine, even when highly diluted, a reddish-brown, amorphous precipitate, which is readily soluble in alcohol, but only very sparingly soluble in acetic acid. The precipitate is readily soluble in potassium hydrate, but it is soon replaced by a white deposit. Dr. W. B. Herapath has shown (*Chem. Gaz.*, 1855, 320) that an alcoholic solution of strychnine yields with iodine, crystalline compounds having very peculiar optical properties.

1. $\frac{1}{100}$ grain of strychnine yields a very copious deposit, which after a time becomes more or less crystalline.
2. $\frac{1}{1000}$ grain: a copious precipitate, which after a time becomes, in part at least, converted into crystals, Plate XI., fig. 4. These crystals are most readily obtained when large excess of the reagent is avoided.
3. $\frac{1}{10,000}$ grain yields a very good precipitate, which readily dissolves to a colorless solution in potassium hydrate, but after a little time the mixture becomes turbid. The precipitate is slowly converted into crystalline nodules.
4. $\frac{1}{50,000}$ grain yields a very satisfactory deposit.
5. $\frac{1}{100,000}$ grain furnishes a very distinct turbidity.

This reagent also produces precipitates with various organic substances, and with certain inorganic compounds, but the character of the strychnine crystals is quite peculiar; their formation, however, is readily interfered with by the presence of foreign matter.

The strychnine may be recovered from the washed precipitate by dissolving the latter in strong alcohol, and treating the solution with slight excess of silver nitrate, which will precipitate the iodine as silver iodide; this is removed by a filter, and the excess of the silver reagent precipitated from the filtrate by the cautious addition

of diluted hydrochloric acid; the silver chloride thus produced is then separated by a filter, and the filtrate evaporated to dryness on a water-bath, when the strychnine will be left in its pure state. This method will serve for the recovery of even extremely minute quantities of the alkaloid.

13. *Bromine in Bromohydric Acid.*

A strong aqueous solution of bromohydric acid saturated with bromine occasions in solutions of salts of strychnine, even when very dilute, a yellow, amorphous precipitate, which is readily soluble in alcohol, and in acetic acid. The precipitate remains amorphous.

1. $\frac{1}{100}$ grain of strychnine yields a very copious, bright yellow deposit, which after a time disappears, but it is reproduced upon further addition of the reagent.
2. $\frac{1}{1000}$ grain yields a copious precipitate.
3. $\frac{1}{10,000}$ grain: a very good deposit.
4. $\frac{1}{50,000}$ grain yields a very satisfactory, yellow precipitate.
5. $\frac{1}{100,000}$ grain yields a distinct turbidity, which after a time disappears, and is not reproduced upon further addition of the reagent.

The reaction of this reagent is common to a large class of organic substances.

14. *Physiological Test.*

Dr. Marshall Hall proposed to take advantage of the extreme sensibility of *frogs* to the effects of strychnine as a means of detecting its presence. He advised to immerse the frog in a solution of the poison; when sooner or later, according to the strength of the solution, the animal is seized with violent tetanic convulsions, in which the extremities become extended to their uttermost and the whole body perfectly rigid. By this method Dr. Hall states that he was enabled to detect 1–5000th of a grain of strychnine. More recently Dr. Harley proposed to inject the strychnine solution into the thoracic or abdominal cavity of the animal; and he states that 1–16,000th of a grain of strychnine acetate introduced into the lungs of a very small frog will render it violently tetanic in about ten minutes.

In the following examinations of this test, about two grains of the strychnine solution were taken up by a pipette, the filled end of

which was then introduced into the stomach of the frog, and the liquid discharged by blowing through the tube. The animals were then placed under an open glass receiver. The frogs were fresh, and varied in weight from fifteen to fifty grains. The results for each quantity of the poison are based upon numerous experiments, and chiefly upon the species of animal known as *Rana Halecina*.

1. 1–100th solution—equal to about 1–50th grain of strychnine—usually produces immediate and violent spasms, and death in about eight minutes.
2. 1–1000th solution: the symptoms generally manifest themselves in three or four minutes, and death usually takes place in from fifteen to thirty minutes.
3. 1–10,000th solution: in some instances the symptoms appeared within ten minutes, while in others they were delayed as long as half an hour.
4. 1–20,000th solution generally produces characteristic symptoms in from thirty to forty-five minutes; but in some few instances the results were not well marked, even after long periods.
5. 1–30,000th solution, or 1–15,000th grain of strychnine: in most instances, especially when very small animals were employed, the symptoms appeared within fifty minutes; but in some cases there were no marked effects, even after some hours.

In applying this test, the frogs should always be fresh from the pond. Occasional agitation of the animal hastens the action of the smaller quantities of the poison; and frequently a violent paroxysm may be induced by a sudden noise, such as clapping of the hands. From experiments made at different times, we are strongly inclined to believe that the sensibility of this animal to the effects of strychnine differs somewhat with the seasons of the year. The spring and early part of the summer seem to be the most favorable for the application of the test. It may be remarked that, in regard to weight, 1–20,000th of a grain of strychnine bears about the same relation to a frog weighing twenty-five grains that two grains do to a man weighing one hundred and forty pounds. When, therefore, the foregoing experiments are taken in connection with the known effects of strychnine upon the human subject, it would appear that the frog is relatively somewhat less sensitive than man to the action of the poison.

This physiological test certainly affords a very valuable means of

corroborating the chemical evidence of the presence of strychnine, and at the same time, as we have just seen, it is extremely delicate; yet it should never be employed to the exclusion of at least some of the chemical tests. In regard to delicacy of action, for the pure alkaloid, it is much inferior to the color test, the latter yielding satisfactory results with a quantity of the poison that would produce no appreciable effect upon a frog, even of the smallest size.

Other Reagents.—*Chlorine gas* passed into somewhat strong solutions of salts of strychnine produces a white, amorphous precipitate. Ten grains of a 1–1000th solution of the alkaloid yield a quite good deposit, which is unchanged upon the addition of ammonia; a similar quantity of a 1–10,000th solution yields a distinct milkiness, which quickly disappears on the addition of ammonia.

Tannic acid, *phosphomolybdic acid*, *phosphoantimonic acid*, *metatungstic acid*, and *Nessler's test* for ammonia also precipitate strychnine from solutions of its salts, even in some instances when very highly diluted. But, as the reactions of these reagents are common to a large class of organic compounds, the results have little or no positive value. *Gallic acid* fails to produce a precipitate, even in highly concentrated solutions of salts of strychnine.

Separation from Organic Mixtures.

From Nux Vomica.—Strychnine may be separated from powdered nux vomica by digesting the powder for some time at a moderate heat with a small quantity of water slightly acidulated with acetic acid; the cooled liquid is filtered, and the filtrate concentrated over a water-bath to a small volume. The concentrated solution, which will have the intensely bitter taste of the alkaloid, is treated with slight excess of potassium or sodium hydrate, and violently agitated with about its own volume of chloroform. After the liquids have completely separated, the chloroform is carefully withdrawn and allowed to evaporate spontaneously in a watch-glass, when the alkaloid will be left usually in its amorphous state, together with more or less foreign matter.

The residue thus obtained may either be examined at once by the chemical tests for strychnine, or be further purified by dissolving it in a very small quantity of acidulated water, rendering the solution alkaline, and again extracting with chloroform. After examining a

portion of the residue by the color test, any remaining portion may be dissolved in a small quantity of water containing a trace of acetic acid, and the solution tested by potassium dichromate, or any of the other liquid tests for the alkaloid.

A single grain of powdered nux vomica, when treated after the above method, will yield very satisfactory evidence of the presence of strychnine. If the nux vomica or vegetable infusion contains a comparatively large proportion of *brucine*, this may interfere with the color reaction of the strychnine. These alkaloids may be separated by one or other of the methods already described.

Suspected Solutions and Contents of the Stomach.—Any organic solids present in the mixture presented for examination are cut into small pieces, and the mass, after the addition of water if necessary, treated with about half its volume of strong alcohol and sufficient acetic acid to give it a distinctly acid reaction. The acidulated mixture is digested at a moderate heat on a water-bath, with frequent stirring, for about half an hour or longer. It is then, after cooling, thrown upon a wet linen strainer, and the solid residue well washed with diluted alcohol and strongly pressed. The mixed strained fluids are concentrated at a moderate temperature to a small volume, again strained, then filtered, and evaporated on a water-bath to about dryness. Any strychnine present will now be in the residue, in the form of acetate, mixed with more or less foreign matter.

The residue thus obtained is thoroughly stirred with a small quantity of water containing a drop of acetic acid, the liquid filtered, the filter washed with a little water, and the mixed filtrates, after concentration if necessary, transferred to a stout test-tube or small bottle, and treated with slight excess of a caustic alkali or its carbonate, when the strychnine will be set free from its saline combination. Should the mixture contain a comparatively large quantity of the alkaloid, the latter may after a time assume the crystalline form. The alkaline mixture is now violently agitated for some little time with something more than its own volume of pure chloroform. When the liquids have fully separated, the supernatant aqueous fluid is transferred, by means of a pipette, to another test-tube, and the chloroform decanted into a glass capsule or watch-glass, care being taken that no remaining drops of the aqueous liquid pass over with the chloroform; the alkaline aqueous mixture is then washed with a fresh portion of chloroform, and this collected with that first em-

ployed. A very good method for separating the last drops of the aqueous liquid from the decanted chloroform is to collect the latter liquid in a dry test-tube and decant it from this into the capsule: the last traces of the former fluid will now usually remain attached to the sides of the tube. If, however, the chloroform has still a milky appearance, the liquid may be passed through a small paper filter, previously moistened with pure chloroform.

The decanted chloroform, which contains any strychnine that was present in the alkaline mixture, is allowed to evaporate spontaneously to dryness. If the liquid contained a very notable quantity of the alkaloid, the latter may remain in its crystalline form: this result, however, is rarely obtained from the first chloroform extract, when operating on the contents of a stomach containing the poison. A portion of the residue may be examined by the color test, as also by the taste; and any remaining portion dissolved in an appropriate quantity of pure water containing a trace of acetic acid, and the solution, after filtration if necessary, examined by some of the liquid tests for strychnine, especially potassium dichromate. If, however, the examination of a small portion of the dry residue should indicate the presence of much foreign matter, the acidulated aqueous solution is rendered alkaline, and again extracted by chloroform, which on evaporation may leave the alkaloid, even when present only in minute quantity, in its crystalline state, or at least sufficiently pure for the application of the more important tests.

On agitating the prepared alkaline solution with chloroform, it sometimes happens that the whole becomes a frothy emulsion, from which the chloroform will not separate, even after several hours. When this occurs, the mixture may be moderately agitated with about half its volume of pure water, and the whole allowed to repose, if necessary, for some hours, when more or less of the water will separate as a highly-colored fluid; this is decanted, and the operation repeated with fresh portions of water so long as the liquid becomes colored. By this means much of the foreign matter will be separated, while any strychnine present will remain in solution in the chloroform mixture, at most only the merest trace of it being taken up by the decanted water. The mixture is now slightly *acidulated* by acetic acid, then transferred to a small dish, and evaporated to dryness on a water-bath; the residue is stirred with a very small quantity of pure water, the solution, after filtration if necessary,

rendered slightly alkaline, and again agitated with fresh chloroform, which will now usually readily separate. Instead of treating the acidulated chloroform mixture in the manner just described, it may be agitated with consecutive portions of pure water as long as this liquid acquires a bitter taste, when the alkaloid will be extracted as strychnine acetate, and be left as such on evaporating the solution to dryness over a water-bath.

On applying the general method now described to the examination of the contents of the stomachs of several different cats, each of which had been killed by *half a grain* of strychnine, we in every instance recovered a very notable quantity of the poison. The only instance in which a quantitative analysis was made was in the case of a young cat, to which the strychnine had been administered in solution upon a very full stomach, and death ensued in ten minutes; the third chloroform extract furnished 11–100ths of a grain of the crystallized alkaloid.

After the same method, from the contents of the stomach of a man who had died from the effects of strychnine, administered, there is every reason for believing, in comparatively small quantity, 18–100ths of a grain of the alkaloid, chiefly in its crystalline state, was recovered. And in another case, in which an unknown quantity of the poison had been administered and death took place in about an hour, 31–100ths of a grain was obtained.

When the chloroform or ether *residue* contains a comparatively large quantity of foreign organic matter, it may fail to respond to the color test for strychnine, even when a very notable quantity of the alkaloid is present, and the residue has an intensely bitter taste. Under these circumstances, the residue may be treated with a few drops of pure *concentrated sulphuric acid*, and heated on a water-bath at 100° C. (212° F.) for some hours, by which the foreign matter will be more or less charred. To the cooled mixture pulverized *barium carbonate* is added in quantity sufficient to very nearly, but *not fully*, neutralize the acid; the mixture is now thoroughly stirred with a little water, the liquid filtered, then rendered alkaline, and the strychnine extracted with chloroform or ether in the usual manner.

After this method we have recovered the alkaloid, in its nearly pure state, from a mixture of 1–1000th grain of strychnine with one grain of animal extractive matter. Under the action of concentrated sulphuric acid at 150° C. (302° F.), in the presence of organic

matter, strychnine may undergo decomposition; *Nordhausen sulphuric acid* decomposes it at 100° C.

Method by Dialysis.—To apply this process, the details of which have heretofore been pointed out (*ante*, p. 427), the organic mixture, acidulated with acetic or hydrochloric acid, is prepared in the manner already described for the examination of the contents of the stomach, and the concentrated solution placed in the *dialyzer*, which is then floated in a dish containing four or five times as much pure water as the volume of fluid to be dialyzed; after twenty-four or thirty-six hours, the *diffusate* is transferred to a porcelain dish, evaporated to dryness on a water-bath, and the residue examined in the ordinary manner.

In regard to the relative merits of this method, even with mixtures containing comparatively large quantities of strychnine, experiments indicate that the *diffusate* usually becomes contaminated to such an extent with foreign matter, that to separate the alkaloid from this requires just the same operations as are required to recover it directly by the ordinary methods from the original mixture; moreover, the relative quantity of the alkaloid that passes into the diffusate, even after twenty-four or thirty-six hours, never exceeds the proportion existing between the volume of liquid in the diffusate and that in the dialyzer. The results of many experiments might be cited in support of the foregoing statements. (See 1st edition *Micro-Chemistry of Poisons*, 583.)

From the Tissues.—For the recovery of *absorbed* strychnine, the soft organ, such as a portion of the liver, is placed in a porcelain evaporating-dish and cut into very small pieces, taking care that none of the fluid present is lost; the mass is rendered sufficiently liquid by water, some strong alcohol added, and the whole well stirred, and acidulated with *sulphuric acid*, in the proportion of about eight drops of the concentrated acid for each fluid-ounce of the mixture. It is then digested at a temperature of about 82° C. (180° F.), with frequent stirring, for half an hour or longer, and, after cooling, strained through a fine linen cloth, the residue washed with acidulated water and strongly pressed.

The strained liquid, including the washings, thus obtained is concentrated on a water-bath, and, when much solid matter has separated, again strained, these operations being repeated until the fluid is reduced to a small volume. This is nearly neutralized with

a fixed caustic alkali or ammonia, taking care, however, that the mixture still retains a very decided acid reaction; then filtered, and the filtrate evaporated, on a water-bath, until only a few drops of liquid remain. When this residue has cooled, it is well stirred with about half an ounce of strong alcohol, which will dissolve, in the form of sulphate, any strychnine present, while the alkali-sulphate, formed from the sulphuric acid and alkali added, together with more or less of the foreign organic matter, will remain undissolved. The alcoholic solution, after filtration, is evaporated on a water-bath to almost dryness, the residue stirred with a small quantity of pure water, and the filtered solution rendered slightly alkaline. It is then agitated with pure chloroform in the usual manner, and this fluid, after careful separation, allowed to evaporate spontaneously.

If on stirring the above nearly dry residue with strong alcohol, for the separation of the strychnine from the alkali-salt, it should form a tenacious gummy mass that will not mix with the liquid,—as is sometimes the case, especially when the subject under examination is the liver,—the fluid is expelled by evaporation, the residue stirred with water, the filtered solution evaporated to nearly dryness, and the residue again treated with alcohol, with which the deposit will now usually readily mix. Again, should the final alkaline solution, when agitated with chloroform, form an emulsion from which the chloroform will not separate, the mixture is treated after one or other of the methods before described for mixtures of this kind. So, also, should the final chloroform residue contain much foreign organic matter, this may be charred by concentrated sulphuric acid at 100° C. in the manner already directed (*ante*, 589).

The *sixth of a grain* of strychnine, in solution, was given to a healthy cat, which had just been fed. Twelve minutes thereafter, the animal was seized with violent tetanic symptoms, and died three minutes later. The liver, together with the contained blood, was then treated after the preceding method. The first chloroform solution thus obtained left on spontaneous evaporation a very small gummy residue, which, when examined in three separate portions by the color test, gave, in each instance, perfectly satisfactory evidence of the presence of strychnine. Although the quantity of the poison thus recovered was even more than sufficient to establish fully its presence by this test, yet it was, probably, too minute to have permitted the reaction of this test being confirmed by any of the other

tests, except by the taste. Whether the strychnine recovered in this instance was simply present in the blood contained in the liver, or whether a portion of it had been deposited in the tissue of this organ, is difficult to decide. None of the other tissues of this animal were examined. An analysis of the gall-bladder and its contents of a similar animal, killed in fifteen minutes by the sixth of a grain of strychnine, failed to reveal the presence of a trace of the poison.

In a case of suspected poisoning by strychnine, in which the person died in forty minutes under violent tetanic convulsions, one hundred and fifty grammes (nearly five ounces) of the liver were preserved in alcohol for three months. The finely-divided tissue, with the alcohol, was then examined after the foregoing method, the chloroform residue being charred with sulphuric acid. The final residue had a yellowish color, was amorphous, and weighed 6–100ths of a grain. Under the action of the color test, about the least visible portion of the residue gave perfectly satisfactory evidence of the presence of strychnine, the reaction being about as well marked as with the pure alkaloid.

For the recovery of strychnine from complex organic mixtures and the tissues, Dr. Th. Chandelon has recently advised (*Zeits. f. Physiol. Chem.*, Nov. 1884, 40) the following method.

The concentrated organic mixture or the finely-divided tissue is mixed with an equal weight of perfectly anhydrous *gypsum*, obtained by heating commercial calcium sulphate in a current of dry air at 130° C. (266° F.) until a portion, on being mixed with water, becomes solid. The gypsum mixture is thoroughly triturated in a mortar, and allowed to stand four or five hours, or until the mass becomes so solid that it may be broken into small fragments. These are placed in a flat porcelain dish on a water-bath or in a drying-oven, and dried at 70° C. (158° F.). The dried lumps are pulverized, and the powder treated with 90 per cent. alcohol to which one gramme of tartaric acid has been added for every one hundred grammes of fresh animal tissue present.

The alcoholic mixture is boiled for a few hours in a flask provided with a condenser to return the alcohol; the cooled liquid is filtered, and the solid residue washed with fresh hot alcohol, this being collected with the first filtrate. The alcoholic liquid, which should be distinctly acid, is distilled in a flask until the principal portion of the alcohol has been expelled, after which the mixture is

evaporated to dryness on a water-bath. The residue is treated with a little boiling water, and the mixture allowed to cool, so that any fatty matter present may separate. The filtered liquid is concentrated to about 20 c.c., then rendered alkaline by sodium hydrate, and mixed on a large watch-glass with sufficient gypsum to render the whole solid. The pulverized mass is dried in a sulphuric acid desiccator, and finally extracted with pure *chloroform* in a Soxhlet apparatus of large size.

The decanted chloroform is concentrated to 10 or 15 c.c., and, if necessary, filtered. It is then treated with an equal volume of a saturated *ethereal* solution of oxalic acid. Crystalline needles and tufts of the oxalate of strychnine will quickly appear, and in a little time the whole of the alkaloid will be thus precipitated. The strychnine oxalate is collected on a filter, washed with a mixture of equal volumes of chloroform and ether, and dried. It is then dissolved in about the least possible quantity of water, and the solution treated with slight excess of ammonia, when the strychnine, in its pure state, will be precipitated in the form of crystalline needles.

On applying this method for the recovery of strychnine in experiments upon a frog and a rabbit, killed by the subcutaneous injection respectively of ten and forty milligrammes of the alkaloid, Dr. Chandelon obtained very satisfactory results. So, also, in some quantitative experiments in which small portions of strychnine were added to large quantities of animal tissue, very nearly the whole of the alkaloid was recovered.

The Blood.—This fluid may be examined for absorbed strychnine in much the same manner as heretofore described for the analysis of the tissues. About four fluid-ounces of the suspected blood, placed in a flask, are treated with an equal volume of water and about half a volume of strong alcohol, then about eight minims of concentrated sulphuric acid added for each ounce of blood, and the whole thoroughly agitated until the mixture becomes perfectly homogeneous. It is then transferred to a dish and heated on a water-bath to near the boiling temperature, with constant stirring, for about fifteen minutes; while still warm, the liquid portion is squeezed through a fine linen cloth, and the black viscid residue washed with alcohol and pressed. Should the whole of the mixture pass through the strainer, as will be the case if too much acid has been added, it is returned to the dish, treated with a few drops of

an alkali, and again heated for a few minutes, then strained. If, on the other hand, the solid matter separated by the strainer, when pressed, is dry and pulverizable, it is returned to the strained liquid, the mixture heated with a few drops more of sulphuric acid, and again returned to the strainer.

The highly colored, turbid liquid thus obtained is now *partially* neutralized with an alkali, concentrated somewhat, and again strained; then *very nearly* neutralized with the alkali, and again heated, when most of the albuminous matter will separate in the form of brownish flakes. These are separated by a linen strainer, washed with diluted alcohol, and strongly pressed. The liquid, which will now usually have only a light brownish color, is concentrated on a water-bath to a small volume, filtered, and evaporated to near dryness. The residue is well stirred with about an ounce of strong alcohol, the liquid filtered, and the solids washed with diluted alcohol. The alcoholic liquid is evaporated to near dryness, the residue thoroughly stirred with a small quantity of pure water, the liquid filtered, then rendered alkaline and extracted with chloroform in the usual manner. In testing the final residue, it should be remembered that at most there is only a very minute quantity of strychnine present.

Absorbed strychnine seems to adhere more tenaciously to the solids of the blood than any of the other ordinary alkaloids, with perhaps the single exception of morphine. For its recovery from this fluid, it is essential that the liquid, after the addition of water and alcohol, be at first acidulated as strongly as possible compatible with the separation of at least a portion of the solid matter. The exact quantity of acid necessary for this purpose will vary somewhat with different samples of blood; it also appears that *sulphuric acid* is better adapted than any other acid for this purpose. If the poisoned blood be acidulated only moderately, as for the recovery of most of the other alkaloids, the whole of the strychnine will usually be separated along with the solid albuminous matter. Before resorting to the method just described, we had followed various methods for the examination of the blood of not less than fifteen different animals killed by strychnine, without in any instance obtaining distinct evidence of the presence of the poison.

On applying this method for the examination of the blood of six different cats and of two dogs, poisoned by comparatively small doses of strychnine, we in every instance obtained perfectly satisfac-

tory evidence of the presence of the alkaloid. In two of these cases, in each of which half a grain of strychnine had been administered to young cats and death took place in three and six minutes respectively, six fluid-drachms of blood from each—the whole that was obtained—furnished residues, about the fifth part of each of which, when examined by the color test, gave unquestionable evidence of the presence of the alkaloid. These instances show the extreme rapidity with which a quite notable quantity of the poison may be absorbed. In fact, in these two cases there was apparently as much strychnine recovered as in those in which life was prolonged for about half an hour.

In none of these experiments did the chloroform leave the strychnine in its crystalline state. But in one of them, after the presence of the poison had been shown in a portion of the residue by the color test, the remaining portion, when stirred with a drop of a very dilute solution of potassium dichromate and the fluid allowed to evaporate spontaneously, furnished a number of octahedral crystals of the chromate of strychnine: this was the only instance in which the residue was thus treated. In every instance the whole of the blood that could be obtained from the animal was examined at one operation. It does not, of course, follow that a given quantity of blood taken from the human subject, poisoned by strychnine, would contain the same amount of the poison as would be present, under like conditions, in a similar quantity of blood from a cat. Indeed, the difference between the smallest fatal dose for the former and that for the latter seems to be very much less than that between the absolute quantities of blood found in each.

In a case of poisoning in the human subject, in which we recovered 14-100ths of a grain of strychnine from the contents of the stomach, about *two ounces* of blood, examined after the above method, furnished satisfactory evidence of the presence of the alkaloid. In this instance, the patient being a man, death took place in about half an hour after the poison had been taken.

On following the method of *Dialysis*, in three different cases, for the examination of the blood of animals poisoned by strychnine, we in no instance detected a trace of the poison in the diffusate. Previously to introducing the blood into the dialyzer, the strongly acidulated fluid was heated for some time with diluted alcohol, then strained and concentrated. On examining the *dialyzed* blood, in one

case, by the method heretofore described, it furnished very distinct evidence of the presence of strychnine.

From the Urine.—Strychnine may be separated from the urine by acidulating the liquid with a few drops of acetic acid, and evaporating it on a water-bath to a thick syrup. When this has cooled, it is well stirred with about a fluid-ounce of nearly absolute alcohol, the liquid filtered, and the residue on the filter washed with similar alcohol, and then strongly pressed. The yellowish filtrate thus obtained is concentrated to a thick syrup, and the residue dissolved in a small quantity of pure water. This solution, after filtration if necessary, is rendered slightly alkaline, by ammonia or either of the fixed alkalies, and agitated in the ordinary manner with pure chloroform, which, after separation, is allowed to evaporate spontaneously, when the alkaloid, if present in very notable quantity, will be left in its crystalline state.

By following this method for the examination of a fluid-ounce of normal urine, to which the 1–100th of a grain of strychnine has been purposely added,—the dilution being one part of the poison in about 50,000 parts of liquid,—the alkaloid may be recovered, in its crystalline form, with scarcely any appreciable loss.

One-fourth of a grain of strychnine, in solution, was given to a very large dog, weighing about eighty-five pounds. Slight tetanic symptoms manifested themselves in about fifteen minutes. These continued for about a quarter of an hour, when a second dose, containing a similar quantity of the poison, was administered. The animal was now soon seized with violent symptoms, but survived the effects of the poison one hour and three-quarters after the administration of the first dose. Five ounces of urine were recovered from the bladder, and treated after the foregoing method; but the examination failed to reveal any distinct evidence of the presence of the alkaloid. A second dog, weighing about sixty pounds, was given a quarter of a grain of the acetate of strychnine. Symptoms appeared in twenty minutes, and after twenty minutes more the animal was found dead. An examination of five and a half ounces of urine obtained from this animal also failed to indicate the presence of strychnine. In this case the urine was strongly acidulated with sulphuric acid, instead of acetic acid, as in the preceding examinations. In an instance, however, in which the above method was employed for the examination of two ounces of bloody urine obtained

from the bladder of a man who had died in one hour and three-quarters from the effects of an unknown quantity of strychnine, the second chloroform residue, when examined by the color test, gave satisfactory evidence of the presence of the alkaloid. According to G. A. Masing, in acute strychnine poisoning the urine invariably yields negative results, but in chronic cases the alkaloid may sometimes be found in this secretion.

FAILURE TO DETECT THE POISON.—It has not unfrequently happened, in fatal poisoning by strychnine, that there was a failure to detect a trace of the poison, even in the contents of the stomach and under circumstances apparently very favorable for its recovery. There is little doubt that some of these failures may be justly attributed to the imperfect methods of analysis employed; yet they have occurred in the hands of the most experienced manipulators. The whole of the poison may be rapidly removed from the stomach by the process of absorption or the act of vomiting, or by these combined; and, in protracted cases, even that which has been absorbed may be entirely eliminated from the body previous to death.

In a case related by Dr. Taylor (*Poisoning by Strychnia*, 151), in which five grains of strychnine, administered by mistake to a lady, proved speedily fatal, not a trace of the poison was found in the contents of the stomach. And in a more recent case, in which an infant two days old was killed in two hours by a teaspoonful of nux vomica, Prof. Hofmann failed to find a trace of strychnine, either in the stomach, intestines, or liver. (*Amer. Jour. Med. Sci.*, April, 1879, 574.) In an instance in which six grains of strychnine had been taken, Prof. Sonnenschein found a quantity of the alkaloid in the stomach; but none was recovered from either the tissues or the blood.

In the case reported by Dr. J. J. Reese, already cited, in which about six grains of strychnine had been taken and life was prolonged for six hours, separate analyses, made *eight weeks* after death, of the contents of the stomach, of the contents of the small intestines, and of the tissues of the stomach and intestines, failed to reveal the presence of a trace of strychnine, either by the taste of the final extract or by the color test. From the quantity of strychnine taken in this instance, and the fact that there seems to have been no vomiting, it was one apparently favorable for the recovery of the poison, especially as the tissues were in a good state of preservation at the

time of the examination. Dr. Reese attributed the failure to the fact that just before death the deceased had taken a quarter of a grain of morphine, which, as we have already seen, has the property of disguising the ordinary reaction of the color test. But, as the final extracts were obtained through the agency of *ether*, in which morphine is almost wholly insoluble, especially in the presence of a free alkali, this explanation can hardly be admitted; moreover, morphine has not the property of concealing the intensely bitter taste of strychnine.

A veterinary surgeon of Bavaria was accused of poisoning his wife with strychnine, she having died under violent tetanic convulsions in two hours after he had given her a "purgative medicine." A chemical examination for strychnine, by Prof. Buchner, of Munich, of the internal organs, removed from the corpse *four months* after burial, furnished absolutely negative results. At the trial, Profs. Dragendorff and Uslar, being called by the defence, declared in the most positive manner that strychnine should always be recovered, even if the body had been buried four months. Owing to these declarations, the accused was acquitted. (*Ann. d'Hyg.*, March, 1880, 278.)

To determine how far these allegations of Profs. Dragendorff and Uslar were true, Profs. Buchner, Gorup-Besanez, and Wislicenus, as chemists, and Prof. Ranke, as physiologist, made a series of experiments upon seventeen dogs, each killed by 0.1 gramme ($1\frac{1}{2}$ grain) of strychnine nitrate (a fatal dose for man). The buried bodies of the animals were variously exhumed and examined at the end of one hundred, one hundred and thirty, two hundred, and three hundred and thirty days. As the result, in all cases the *chemical tests failed* to reveal the presence of strychnine. Nevertheless, in every instance, even in the dog exhumed at the end of three hundred and thirty days, the presence of the poison could be inferred from the *bitter taste* of the obtained product. Moreover, the extracts obtained by each of the chemists, and in which strychnine could not be discovered chemically, when dissolved and injected into *frogs*, caused within a few minutes violent tetanic convulsions. These convulsions were the more rapid and intense in proportion to the shortness of time the dogs were buried, being, however, still very evident in the extract from the dog buried three hundred and thirty days. (*Ann. d'Hyg.*, April, 1881, 385.)

In a case we examined in 1875, in which a woman was suddenly seized with violent tetanic convulsions, and died within two hours under most marked symptoms of strychnine poisoning, the stomach with its contents and a portion of the liver, examined *seven months* after death, furnished extracts having an intensely *bitter taste;* but in no instance did the chemical tests for strychnine yield satisfactory evidence of the presence of the poison. The husband of the deceased was tried for the poisoning, and found guilty of murder in the second degree. (*State of Ohio* v. *J. Dresbach,* 1881.) In another case, we readily found strychnine in the stomach of a child that had died from the effects of the alkaloid, and in which the organ was removed from the exhumed body two weeks after death, and preserved in alcohol five weeks longer.

Although in experiments upon animals and in preserved organic mixtures, strychnine has been repeatedly found after very long periods, yet the longest period in which the analysis furnished positive evidence of its presence in the *exhumed human body* is forty-three days after death. (*Ann. d'Hyg.*, April, 1881, 359.) In a body in which the examination was made nearly four months, and in another something over a year, after burial, no trace of the poison was found.

In a case reported by Dr. A. A. Hayes, he recovered over half a grain of crystallized strychnine from the fourth part of the contents of the stomach two weeks after death, the post-mortem having been made ten days after death. In this instance as much as twenty grains of strychnine may have been taken. (*Boston Med. and Surg. Jour.*, March, 1861, 133.) Strychnine has also been recovered from the human subject after three weeks, one month, and at the end of five weeks. (*Ann. d'Hyg.*, April, 1881, 354.)

At the trial of Mary Freet, charged with the murder of her husband by strychnine, it was alleged that a few weeks prior to the administration of the fatal dose the defendant prepared a bowl of mush and milk for the deceased, and that he complained of its having a bitter taste, and threw the contents of the bowl into the yard; and that afterward a cat having eaten the mush very suddenly died. A chemical examination of the contents of the stomach of the animal two months after death, the body having part of the time been exposed in a common alley, clearly revealed the presence of strychnine.

Quantitative Analysis.—The quantity of strychnine present in a pure aqueous solution of any of its salts may be estimated with sufficient accuracy for ordinary purposes by treating the somewhat concentrated solution with slight excess of a caustic alkali, and allowing the mixture to stand in a cool place for from twelve to twenty-four hours, when the deposit will have assumed the crystalline form. The precipitate is then collected on a small equipoised filter, washed with a small quantity of cold water, dried on a water-bath, and weighed. Since strychnine is not wholly insoluble in water, even in the presence of a free alkali, a minute portion of the alkaloid will remain in the alkaline liquid. The quantity, however, that may thus escape precipitation will rarely exceed the 1–10,000th part by weight of the fluid present. If on extracting the alkaloid from its aqueous solution by means of chloroform or ether, it is left, on evaporation of the liquid, in its pure state, it may, of course, be at once weighed. One hundred parts by weight of the alkaloid correspond to about 133 parts of the pure crystallized sulphate, 118 parts of the acetate, or about 120 parts of crystallized hydrochloride of strychnine.

III. Brucine.

History.—Brucine, or *brucia,* occurs in most if not all of the Strychnos plants in which strychnine is found. It was first discovered, in 1819, by Pelletier and Caventou, in what was formerly known as false Angustura bark, but which has since been shown to be the bark of the nux vomica tree. It occurs both in the bark and seed of this tree; in the bark—which contains less strychnine and more brucine than the seed—it is said to be in combination with gallic acid, while in the seed it is believed to be combined with strychnic acid. The proportion of brucine in nux vomica is said to vary from 0.12 to 1.10 per cent. The composition of the anhydrous alkaloid, according to Regnault, is $C_{23}H_{26}N_2O_4$.

Preparation.—Brucine may be obtained from the bark of nux vomica in a manner similar to that by which strychnine is obtained from the seed, except that the alcoholic extract obtained from the precipitate produced by lime is treated with oxalic acid, and subsequently with a mixture of alcohol and ether, which dissolves the coloring matter, while the oxalate of brucine remains undissolved. This salt is then decomposed by magnesia, and the liberated brucine

dissolved in alcohol, which on spontaneous evaporation leaves the alkaloid in its crystalline state.

Physiological Effects.—The effects of brucine on the animal economy are precisely the same in kind as those of strychnine; but it is less energetic in its action than the latter alkaloid, having only about one-twelfth the power of that substance. Dr. Christison cites two instances of poisoning by this substance; and Prof. Casper relates three cases in which death resulted from the taking of a mixture of arsenic and brucine. (*Forensic Medicine*, ii. 102.) In a case related by Dr. T. S. Sozinskey (*Med. and Surg. Rep.*, Aug. 1882, 194), two grains of brucine taken by a man produced most alarming symptoms, essentially the same as those produced by strychnine: under active treatment the patient entirely recovered. The ordinary medicinal dose of brucine is from half a grain to one grain, repeated two or three times a day.

General Chemical Nature.—Brucine is a white, odorless solid, having an intensely bitter taste, very similar to that of strychnine. In its pure state it is readily crystallizable, forming beautiful groups of very delicate, transparent needles; when the crystals are only slowly produced, they usually appear in the form of bold, colorless, four-sided prisms: the crystals contain four molecules, or about 15.45 per cent. of their weight, of water of crystallization, their composition being $C_{23}H_{26}N_2O_4,4H_2O$. When moderately heated, the crystals fuse and become anhydrous; and at a higher temperature the residue takes fire and burns with a dense smoky flame. Brucine may be sublimed unchanged. According to Prof. Guy, the alkaloid fuses at 115.5° C. (240° F.) and sublimes at 204.4° C. (400° F.), the sublimate being generally amorphous. (*Forensic Medicine*, 1881, 576.) Brucine is unacted upon by the fixed caustic alkalies, but it is readily decomposed by concentrated nitric acid.

The *salts* of brucine are colorless, except when they contain a colored acid, and are for the most part easily crystallizable. They have the bitter taste of the pure alkaloid, and are readily decomposed by the caustic alkalies, with the elimination of the brucine. In regard to its basic properties, brucine is somewhat inferior to strychnine, it being displaced from its saline combinations by that alkaloid.

Solubility.—When excess of pure powdered brucine is frequently agitated with *pure water* at the ordinary temperature for twenty-four

hours, one part of the crystallized alkaloid dissolves in 900 parts of the liquid: this corresponds to one part of the anhydrous alkaloid in about 1050 parts of the menstruum. It is much more soluble in hot water, from which, however, the greater part of the excess separates as the solution cools. Its solubility in this liquid is somewhat increased by the presence of foreign organic matter.

Absolute ether, when frequently agitated for several hours at the ordinary temperature with excess of the powdered alkaloid, dissolves one part of the anhydrous base in 440 parts of the liquid. *Chloroform* readily dissolves the alkaloid in nearly every proportion. It is thus obvious that this liquid is better adapted than ether for the separation of the alkaloid from alkaline aqueous mixtures. The alkaloid is also readily soluble in nearly every proportion in *absolute alcohol*. But it is insoluble in the fixed caustic alkalies, and only sparingly soluble in large excess of ammonia. Most of the *salts* of brucine are freely soluble in water and in alcohol.

Special Chemical Properties.—Concentrated *sulphuric acid* dissolves brucine and its salts with the production of a faint rose-red color. If the acid contains nitric acid—as is frequently the case—the alkaloid dissolves to a deep red solution. If a small crystal of potassium dichromate be stirred in the sulphuric acid solution, the liquid acquires an orange or brownish-orange color, which slowly changes to a greenish hue, due to the separation of chromium oxide. This reaction at once distinguishes brucine from strychnine. Concentrated *nitric acid* dissolves the alkaloid, as well as its salts, to a deep red solution, the color of which slowly fades to yellow. The statement of Sonnenschein, that under the action of nitric acid brucine is converted into strychnine, has not been confirmed by more recent observers. Brucine is readily soluble in concentrated *hydrochloric acid* without change of color.

In the following examination of the reactions of solutions of brucine, the pure crystallized alkaloid was dissolved, by the aid of just sufficient acetic or sulphuric acid, in pure water. The fractions employed indicate the fractional part of a grain of the crystallized alkaloid in solution in one grain of water; and the results, unless otherwise indicated, refer to the behavior of one grain of the solution. One grain of pure crystallized brucine corresponds to 0.845 of a grain of the anhydrous alkaloid.

1. *The Caustic Alkalies.*

The fixed caustic alkalies and ammonia produce in concentrated solutions of salts of brucine a white, amorphous precipitate of the pure anhydrous alkaloid, which after a little time, by the assimilation of water, assumes the crystalline form. The precipitate is readily soluble in free acids, even in acetic acid; but it is insoluble in large excess of either potassium or sodium hydrate. In its amorphous state the precipitate is rather freely soluble in large excess of ammonia; but when it has assumed the crystalline form it is only very sparingly soluble in that liquid.

1. $\frac{1}{100}$ grain of brucine, in one grain of water, yields with either of the fixed alkalies an immediate amorphous precipitate, which in a very little time gives rise to very beautiful groups of exceedingly delicate crystalline needles, Plate XI., fig. 5; and soon the mixture becomes converted into a nearly solid mass of crystals. Ammonia produces a similar precipitate, but it does not usually appear until after some little time; it then separates in the crystalline form. If large excess of ammonia be added, the precipitate may fail to appear, even after several hours.
2. $\frac{1}{500}$ grain yields with a fixed alkali an immediate cloudiness, and soon a very good crystalline precipitate. The formation of the precipitate is much facilitated by stirring the mixture. Very similar results may be obtained by ammonia, provided it be added in very minute quantity.

Solutions of salts of brucine but little more dilute than the last-mentioned fail to yield a precipitate by either of the caustic alkalies.

The *alkali carbonates* behave with solutions of salts of brucine in much the same manner as the free alkalies. The true nature of the precipitate produced by the caustic alkalies may be confirmed by either of the two next-mentioned tests.

2. *Nitric Acid and Stannous Chloride.*

If a few crystals of brucine or of any of its colorless salts, in the dry state, be treated with a drop of concentrated nitric acid, they immediately assume a deep *blood-red color*, and quickly dissolve to a solution of the same hue; on heating this solution its color is changed to orange-yellow or yellow. If, when the solution has cooled, a drop of a solution of stannous chloride be added, the mixture immediately

acquires a beautiful *purple* color, which is discharged by large excess of either nitric acid or of the tin compound, as also by sulphurous oxide gas. The red color of nitric acid solutions of brucine containing a quite notable quantity of the alkaloid is changed to a faint purple on the addition of the tin solution alone, without the application of heat: but the intensity of the color, as thus obtained, is much inferior to that obtained from the brucine solution after it has been heated; and if only a minute quantity of the alkaloid be present, without the application of heat, the purple color entirely fails to appear.

The following quantities of brucine were obtained by evaporating one grain of the corresponding solution of the acetate to dryness on a water-bath.

1. $\frac{1}{100}$ grain of brucine dissolves in a drop of nitric acid to a deep red solution, which, when heated and allowed to cool, and then treated with the tin compound, acquires an intense purple color.
2. $\frac{1}{1000}$ grain: the drop of acid acquires a very satisfactory red color, which upon the addition of the tin salt, after the solution has been heated, is changed to a beautiful lilac.
3. $\frac{1}{10,000}$ grain: on the addition of a very small drop of the acid the deposit assumes a very decided red color, and dissolves to a faint red solution; the tin salt produces a quite distinct lilac coloration. To obtain the latter color the acid and tin compound must be well apportioned, otherwise the reaction may entirely fail to manifest itself. This is about the limit of the tin reaction.
4. $\frac{1}{50,000}$ grain, when moistened with a minute trace of the acid, assumes a quite perceptible red color; if this mixture be evaporated to dryness, on a water-bath, it leaves a very satisfactory red deposit.
5. $\frac{1}{100,000}$ grain, when treated as under 4, leaves a quite distinct red residue.

These reactions of nitric acid and stannous chloride, when taken in connection, are quite characteristic of brucine; and at the same time, as we have just seen, are exceedingly delicate. In these respects this test bears much the same relation to brucine that the color test does to strychnine. Nitric acid also produces a red color with morphine and with several other substances besides brucine; but the subsequent addition of stannous chloride fails to produce, with any of these fallacious solutions, a purple coloration. The red color

of the acid solution of morphine is but little affected by the tin compound, at most being changed to yellow; when the acid solution has been heated and allowed to cool, the tin salt produces no visible change.

3. *Sulphuric Acid and Potassium Nitrate.*

Brucine and its salts, as already pointed out, dissolve in concentrated sulphuric acid with the production of a rose-red color. If a crystal of potassium nitrate be stirred in the solution, the mixture acquires a deep orange-red color, due to the action of the nitric acid of the nitre. This test, therefore, is very similar in its action to the one just considered.

1. $\frac{1}{100}$ grain of brucine, when treated with a small drop of concentrated sulphuric acid, dissolves to a solution having a faint rose color, which on the addition of a small crystal of nitre is changed to deep orange-red.
2. $\frac{1}{1000}$ grain: on the addition of the acid the deposit assumes a quite perceptible rose-red color, and dissolves to a colorless solution, which on the addition of the nitre acquires a beautiful orange color.
3. $\frac{1}{10,000}$ grain: the acid dissolves the deposit with little or no change of color; but the solution, when treated with the potassium salt, acquires an orange color, which soon changes to yellow.
4. $\frac{1}{25,000}$ grain: when the acid solution is treated with the nitre it yields only a faintly yellow coloration. But if a small crystal of nitre be moistened with the acid and then stirred over the dry brucine deposit, the crystal acquires a distinct orange color.

The production of these colors is quite peculiar to brucine. Sulphuric acid solutions of narcotine, opianyl, and morphine, when treated with potassium nitrate, yield colors somewhat similar to that produced from brucine; but neither of these substances dissolves in the acid with the production of a rose-red color.

4. *Potassium Sulphocyanide.*

This reagent throws down from quite concentrated solutions of salts of brucine a white precipitate of brucine sulphocyanide, which is insoluble in acetic acid. As produced from very concentrated solutions, the precipitate is in the amorphous form, but it soon becomes more or less crystalline. From somewhat more dilute solutions the

precipitate does not appear until after some time, and it then separates in the form of small granules. The formation of the precipitate from solutions of this kind is much facilitated by stirring the mixture with a glass rod.

One grain of a 1–100th solution of the alkaloid yields no immediate precipitate, but in a few moments comparatively large groups of minute granules appear, and after a few minutes there is a quite good deposit of these groups, with occasionally small transparent crystalline plates, Plate XI., fig. 6. A similar quantity of a 1–500th solution fails to yield a precipitate, even when the mixture is allowed to stand for some hours.

5. *Potassium Dichromate.*

Potassium dichromate throws down from solutions of salts of brucine, even when highly diluted, a yellow precipitate of brucine chromate, which is insoluble in acetic acid. The precipitate is readily soluble, with the production of a deep red color, in concentrated nitric acid, and in sulphuric acid, with the production of a reddish-brown color.

1. $\frac{1}{100}$ grain of brucine, in one grain of water, yields a quite copious amorphous precipitate, which in a few moments becomes converted into crystalline groups of the forms illustrated in Plate XII., fig. 1.
2. $\frac{1}{1000}$ grain: if the mixture be stirred, it immediately yields streaks of granules and small crystals along the path of the rod, and in a little time there is a quite copious crystalline deposit.
3. $\frac{1}{5000}$ grain yields after a little time, especially if the mixture has been stirred, a quite satisfactory crystalline precipitate.
4. $\frac{1}{10,000}$ grain: after several minutes a quite distinct precipitate, and after about half an hour a very satisfactory deposit of crystalline needles.

The crystalline form of the precipitate, as produced from somewhat strong solutions of the alkaloid, together with the subsequent reaction of nitric acid, serves to distinguish the chromate of brucine from all other precipitates produced by this reagent.

Potassium monochromate produces in solutions of the alkaloid results very similar to those occasioned by the dichromate, only that the reaction is not quite so delicate.

6. *Platinic Chloride.*

Solutions of salts of brucine yield with platinic chloride a yellow precipitate of the double chloride of platinum and brucine, $2C_{23}H_{26}N_2O_4,HCl\,;PtCl_4$, which is unchanged by acetic acid, but readily decomposed by the caustic alkalies.

1. $\frac{1}{100}$ grain of brucine yields a very copious deposit, which almost immediately becomes a mass of irregular crystalline needles. The precipitate is slowly soluble in nitric acid, yielding an orange-red solution.
2. $\frac{1}{1000}$ grain: an immediate light yellow, crystalline precipitate, which in a little time becomes converted into irregular needles, Plate XII., fig. 2.
3. $\frac{1}{5000}$ grain: very soon crystals appear, and after a little time there is a quite good crystalline deposit.
4. $\frac{1}{10,000}$ grain: if the mixture be stirred, it immediately yields crystalline streaks, and very soon a quite fair deposit.
5. $\frac{1}{25,000}$ grain: after a few minutes, if the mixture has been stirred, crystalline needles appear, and after a little time there is a quite satisfactory deposit.

This reagent also produces yellow crystalline precipitates with various other substances, but the form of the brucine deposit is somewhat peculiar.

7. *Auric Chloride.*

This reagent produces in solutions of salts of brucine a yellow, amorphous precipitate which has the composition $C_{23}H_{26}N_2O_4,HCl$, $AuCl_3$, and which in a little time acquires a flesh color. The precipitate is but sparingly soluble in acetic acid; the caustic alkalies cause it quickly to assume a dark color.

1. $\frac{1}{100}$ grain of brucine, in one grain of water, yields a very copious deposit.
2. $\frac{1}{1000}$ grain yields a greenish-yellow precipitate, which soon becomes yellow; the deposit is readily soluble to a clear solution in potassium hydrate.
3. $\frac{1}{10,000}$ grain: a quite good, yellowish deposit.
4. $\frac{1}{25,000}$ grain yields in a very little time a distinct turbidity, and after a few minutes a quite satisfactory precipitate.
5. $\frac{1}{50,000}$ grain: after some minutes a quite distinct deposit.

All these precipitates remain amorphous. The reaction of this reagent is common to a large class of substances.

8. *Picric Acid.*

An alcoholic solution of picric acid throws down from aqueous solutions of salts of brucine a yellow precipitate of brucine picrate, which is but sparingly soluble in large excess of acetic acid.

1. $\frac{1}{100}$ grain of brucine yields a very copious precipitate, which after a time becomes, in part at least, crystalline. The formation of these crystals is readily prevented by the presence of foreign organic matter.
2. $\frac{1}{1000}$ grain yields a very good precipitate, which after a time is converted into groups of aggregated granules, similar to those produced by potassium sulphocyanide (Plate XI., fig. 6).
3. $\frac{1}{10,000}$ grain yields after several minutes, especially if the mixture has been stirred, a quite distinct precipitate.

The reaction of this reagent is valuable only in so far as it confirms the reactions of the other tests for brucine.

9. *Potassium Ferricyanide.*

Concentrated neutral solutions of salts of brucine, when treated with this reagent, yield a light yellow, crystalline precipitate, which is readily soluble in the mineral acids. The formation of the precipitate is readily prevented by the presence of a free acid, even of acetic acid, but after the crystals have formed they are only very sparingly soluble in large excess of acetic acid.

1. $\frac{1}{100}$ grain of brucine yields an immediate precipitate, and in a few moments there is a very copious deposit of crystals, grouped in various and most beautiful forms, Plate XII., fig. 3. These crystalline groups are, perhaps, the most brilliant polariscope objects yet known. The production of these crystals is quite characteristic of brucine.
2. $\frac{1}{500}$ grain: after stirring the mixture it yields in a very little time a copious granular deposit.
3. $\frac{1}{1000}$ grain: after some time a slight turbidity.

Potassium ferrocyanide produces no precipitate with a 1–100th solution of brucine, even if the mixture be allowed to stand for some time.

10. *Iodine in Potassium Iodide.*

A solution of iodine in potassium iodide produces in normal solutions of salts of brucine, even when very highly diluted, an orange-brown, amorphous precipitate, which is insoluble in acetic acid.

1. $\frac{1}{100}$ grain of brucine yields a very copious deposit, which is decomposed by large excess of potassium hydrate, with the production of a dirty-white precipitate.
2. $\frac{1}{1000}$ grain: much the same results as 1.
3. $\frac{1}{10,000}$ grain yields a quite good, brownish precipitate, which is soluble to a clear solution in a caustic alkali.
4. $\frac{1}{50,000}$ grain yields a yellowish deposit.
5. $\frac{1}{100,000}$ grain: a very distinct, dirty-yellowish turbidity.
6. $\frac{1}{500,000}$ grain yields a perceptible cloudiness.

It need hardly be remarked that this reagent produces similar precipitates in solutions of most of the alkaloids and of various other organic substances.

11. *Bromine in Bromohydric Acid.*

A strong aqueous solution of bromohydric acid saturated with bromine produces in solutions of salts of brucine, when not too dilute, a deep brown, amorphous precipitate, which after a time dissolves, but is reproduced upon further addition of the reagent. The precipitate is soluble in acids, even acetic acid, and in potassium hydrate.

1. $\frac{1}{100}$ grain of brucine yields a very copious, deep brown deposit, which soon acquires a yellow color, then a bright yellow, and after some minutes dissolves.
2. $\frac{1}{1000}$ grain: much the same results as 1.
3. $\frac{1}{10,000}$ grain yields a yellowish precipitate, which after a time disappears, and is not reproduced upon further addition of the reagent.
4. $\frac{1}{20,000}$ grain yields a greenish-yellow deposit, which soon dissolves.

The brown color of the brucine deposit distinguishes it from the precipitates produced by this reagent with other alkaloids.

Other Reactions.—S. Cotton has shown that when a *warmed* nitric

acid solution of brucine is treated with a concentrated solution of *sodium hydrosulphide*, the mixture assumes a beautiful *violet* color, which is changed to *green* by large excess of the reagent. This color is not affected by the alkalies, but diluted acids change it to rose-red, sulphuretted hydrogen being evolved. (*Jour. Pharm. et Chim.*, July, 1869, 18.) The reagent may be prepared by saturating a strong solution of sodium hydrate (1 : 8) with sulphuretted hydrogen gas.

To apply this test, a few drops of the brucine solution, placed in a small test-tube, are treated with a few drops of nitric acid, the mixture warmed to 40° or 50° C. (about 115° F.), and then a drop or two of the reagent added. In this manner a 1–1000th solution of brucine will yield a deep violet coloration, which under excess of the reagent is changed to green. A 1–10,000th solution yields a very good violet or purple coloration, passing to deep green under excess of the reagent. Even a 1–100,000th solution will yield a distinct purple, followed by a perceptible green coloration. Strychnine yields no color under this test, and morphine fails to yield a similar coloration.

Mercurous nitrate, free from excess of nitric acid, occasions no coloration with solutions of salts of brucine in the cold; but if the mixture be heated on a water-bath, a beautiful *carmine* color is gradually developed, which is permanent on evaporating the liquid to dryness. This coloration is very intense in a few drops of a 1–100th solution of brucine; and the *residue* from a similar quantity of a 1–10,000th solution has a well-marked pinkish hue. According to F. A. Fluckiger, who first observed this reaction, strychnine, the alkaloids of opium and cinchona, veratrine, caffeine, and piperine, produce no color under these conditions; but albumin and phenol yield similar colorations.

Prof. Dragendorff has lately shown (1878) that if brucine be dissolved in diluted sulphuric acid (1 : 10), and a minute quantity of a very dilute aqueous solution of potassium dichromate be then added, the mixture acquires a beautiful red color, changing to reddish-orange, then to brownish-orange, the reaction being one of oxidation. Under this reaction a coloration will manifest itself, as claimed by Dragendorff, in a 1–10,000th solution of the alkaloid.

According to Watson Smith, if solid brucine be let fall upon *antimony trichloride* heated to fusion, a beautiful red or purple-red

color is developed, even when only the minutest trace of the alkaloid is employed. (*Chem. News*, July, 1879.) Mr. Smith states that this reaction is peculiar to brucine.

Corrosive sublimate throws down from a 1–100th solution of salts of brucine a quite good, white, amorphous precipitate, which soon becomes granular; with solutions but little more dilute than this the reagent fails to produce a precipitate. *Potassium iodide* produces in a 1–100th solution of the alkaloid no immediate precipitate, but after a time there is a quite good deposit of rough needles and crystalline plates. *Tannic acid* throws down from even highly diluted solutions of the alkaloid a dirty-white, amorphous precipitate, which is soluble in acetic acid.

Chlorine gas passed into concentrated solutions of salts of brucine produces at first a yellow, then a red color, which is discharged by excess of the gas. Upon the subsequent addition of ammonia, the liquid acquires a light brown color. These reactions manifest themselves only in very strong solutions of salts of the alkaloid.

Administered to *frogs*, brucine produces violent tetanic convulsions, similar to those occasioned by strychnine, but their production requires relatively a much larger quantity of the former than of the latter alkaloid.

Since the symptoms produced by strychnine and brucine are so very similar in their nature, the examiner should bear this in mind in a case of suspected poisoning, especially when the tests for the former alkaloid have failed to show its presence.

Separation from Organic Mixtures.

Brucine may be separated from organic mixtures in the same manner as heretofore directed for the recovery of strychnine. When the analysis furnishes only a small residue for the application of the chemical tests, a portion of it should first be examined by the nitric acid and stannous chloride test. If this yields a positive reaction, it fully establishes the presence of the alkaloid. When, however, sufficient material is at hand, the reaction of this test should be confirmed by some of the other tests. Should the nitric acid and tin test fail, it is quite certain that, under similar conditions, the other tests would also fail.

One grain of brucine in solution was given to a recently fed cat; thirty minutes afterward, the animal was seized with violent tetanic

convulsions and died during the paroxysm. On now applying the method directed for the recovery of strychnine to the examination of the contents of the stomach of the animal, a very notable quantity of pure crystallized brucine was recovered. And six fluid-drachms of blood, taken from the same animal and treated after the strychnine-method, gave, when the first chloroform residue was examined by the tin test, perfectly satisfactory evidence of the presence of brucine.

According to M. Pander, this alkaloid, when taken into the system, is widely distributed, and may be found in all the tissues and fluids of the body, especially in the liver and kidneys; and decomposition of the tissues for at least three months does not destroy the brucine.

CHAPTER IV.

ACONITINE, ATROPINE, DATURINE.

Section I.—Aconitine. (Aconite.)

History.—*Aconitine, aconitina,* or *aconitia,* is the active principle, or alkaloid, of Aconite, Monkshood, or Wolfsbane, the *Aconitum Napellus* of botanists. It exists in all parts of the plant, but in the greatest proportion in the root, being combined with *aconitic* or *equisetic* acid. The dried root is usually estimated to contain from 0.1 to 0.2 per cent. of the alkaloid. Aconitine was first obtained, although in an impure state, by Geiger and Hesse, in 1832. Planta assigned to the alkaloid the formula $C_{30}H_{47}NO_7$; but, according to Dr. C. R. A. Wright, its composition is $C_{33}H_{43}NO_{12}$. In its pure state aconitine is perhaps the most potent poison yet known. According to Dr. Wright, ordinary aconite sometimes contains another alkaloid, having the composition $C_{31}H_{45}NO_{10}$, named *picraconitine,* which has a bitter taste, is uncrystallizable, and comparatively inert.

It was formerly believed that the activity of the different species of aconite was chiefly due to the presence of the same alkaloid—namely, aconitine. According to the researches of Dr. Wright, however, the corresponding crystallizable principle in *Aconitum ferox,* named *Pseudaconitine,* has the composition $C_{36}H_{49}NO_{12}$; whilst the roots of *Japanese aconite* owe their activity chiefly to *Japaconitine,* $C_{66}H_{88}N_2O_{21}$, these roots being considerably richer in active crystallizable principles, as also in non-crystalline bases, than the ordinary root. (*Jour. Chem. Soc.,* 1877, 403.) Experiments would indicate that in their physiological effects *aconitine, pseudaconitine,* and *japaconitine* are at least very similar, if not identical. So, also, the three alkaloids appear to have the same general chemical properties.

Preparation.—Various methods have been proposed for the

preparation of *aconitine*. The following process was advised by MM. Liégeois and Hottot. The bruised root of the plant is digested for eight days with rectified spirit, slightly acidulated with sulphuric acid; the alcoholic liquid is then pressed out, and the alcohol removed by distillation. The residue is allowed to cool, and any solid resinous matter that separates removed. The liquid is now concentrated to the consistency of a syrup, then treated with two or three volumes of pure water, and the mixture allowed to repose, as long as any green oil collects upon its surface; this is removed, the last traces being separated by a filter previously moistened with water. The liquid is next treated with slight excess of magnesium hydrate, and repeatedly agitated with pure ether, which will extract the alkaloid. The united ethereal extracts are evaporated to dryness, and the residue dissolved in water by the aid of slight excess of sulphuric acid. The alkaloid is then precipitated from the filtered solution by slight excess of ammonia, and further purified by repeated solution in water acidulated with sulphuric acid and re-precipitation by ammonia. The final precipitate is washed with cold water as long as any odor of ammonia is present, then dried at a low temperature.

According to Duquesnel, *crystallized aconitine* may be obtained by the following method. Powdered aconite root is mixed with one per cent. of tartaric acid, and extracted by three successive portions of alcohol. The united and filtered liquids are distilled at a low temperature to an extract, the extract treated with water, and the fatty and resinous matter separated by filtration. The filtrate, which contains the alkaloid as tartrate, is repeatedly shaken with ether, to deprive it of coloring matter; slight excess of acid potassium carbonate is then added, and the liberated alkaloid extracted by ether. The ethereal liquid is shaken with a ten per cent. solution of hydrochloric acid, which takes up the alkaloid as hydrochloride, the extraction with the acid liquid being repeated two or three times with fresh portions of the liquid. The united acid liquids are saturated with chalk, then concentrated at a gentle heat, filtered, and, while still warm, mixed with a strong solution of *sodium nitrate*. This mixture is allowed to cool slowly, when the alkaloid, in the form of nitrate, will separate in its crystalline state. The nitrate thus obtained is dissolved in water, the solution treated with slight excess of acid potassium or ammonium carbonate, and the freed alkaloid extracted by chloroform. On evaporation, the chloroform will leave

a syrupy liquid, which will soon crystallize, especially if the syrup be treated with an equal volume of alcohol.

The total quantity of active alkaloids obtained from aconite root has varied greatly, depending upon the process followed for the extraction, the product ranging, according to M. Schneider, from 0.002 to 0.34 per cent. of the root. So, also, great variation exists in the strength of samples of the alkaloid as found in the shops. From a comparative examination of some of the well-known commercial preparations of aconitine, Prof. P. C. Plugge concluded that Petit's nitrate has a toxic action at least eight times greater than that of Merck, and one hundred and seventy times greater than that of Friedländer. Morson's aconitine is said to be about equal in activity to that of Petit.

Poisoning by *aconitine* in its *pure state* has been of rare occurrence; but there have been numerous instances of poisoning by the root, leaves, and some of the preparations of *aconite*, chiefly, however, as the result of accident. The root has not unfrequently been mistaken for horseradish. The principal pharmaceutical preparations of aconite are the tincture of the root and the alcoholic extract. Each of these preparations is subject to considerable variation in strength, depending both on the formula followed for its preparation and on the quality of the material employed. The medicinal dose of the pure alkaloid is said to be about the 1–130th of a grain: it is rarely prescribed in this form, and requires great caution in its administration.

Symptoms.—The effects of poisonous doses of aconite are in some respects quite peculiar. At first there is a sense of tingling and numbness in the lips, mouth, and throat, with a feeling of warmth or burning in the stomach. These effects are succeeded by tingling in various parts of the body, pain in the abdomen, headache, vertigo, and nausea, frequently attended by vomiting, and sometimes purging; there is, also, diminished sensibility of the skin, constriction in the throat, frothing at the mouth, partial or entire loss of voice, impaired vision, ringing in the ears, a feeling of tightness in various parts of the body, cold perspirations, muscular tremors, and great prostration of strength. The pulse becomes small and feeble, or altogether imperceptible; the countenance pale and sunken; the extremities cold and clammy: the pupils are usually dilated, but not

unfrequently contracted. Death usually takes place by syncope. In some instances death is preceded by delirium and convulsions. In fifty-three cases of aconite poisoning collected by Dr. Tucker, of New York, general convulsions occurred only in seven; and in forty-one cases collected by Dr. E. T. Reichert (*Med. Times*, Nov. 1881, 105), general convulsions were present only in three instances.

The symptoms usually manifest themselves within a few minutes after the poison has been taken; but they have been delayed for more than an hour, and in one case for even more than three hours. In a case quoted by Dr. Beck (*Med. Jur.*, ii. 890), in which a man had eaten some salad containing, by mistake, a quantity of aconite, the patient *immediately* experienced a burning heat in the tongue and gums, and irritation in the cheeks. This tingling sensation extended over the whole body, and was accompanied by muscular twitchings. The eyes and teeth became fixed; the extremities cold and bathed with perspiration; the pulse imperceptible, and the breathing so short as scarcely to be distinguishable. Under the active use of remedies the patient gradually recovered. In another case, a woman on swallowing an alcoholic tincture of the root immediately experienced a tingling sensation in her lips, mouth, and tongue; her teeth felt as if loose, and her lower jaw as if dead. Tingling then began in her fingers and extended all over her body, and she felt numb. She finally recovered. (*Med. Times*, Feb. 1879, 241.)

In a case reported by Dr. Gray, in which a healthy boy, fourteen years of age, was given by mistake a tablespoonful of the tincture of aconite, the following symptoms were observed. In about five minutes the patient began to experience the effects of the poison, and in twenty minutes the pupils were slightly dilated and nearly insensible to light; the countenance was pale, and he moved with difficulty; his head felt heavy, and there was frequent retching, with the discharge of small quantities of mucus. An emetic of zinc sulphate was immediately administered, and quickly produced copious vomiting. The patient now experienced a sense of intense burning in the stomach and œsophagus, and was greatly prostrated; the pulse became slow, the extremities cold, the pupils widely dilated, and he complained of great numbness of his head, but not of any other part of the body, and lost the power of sight. Under the use of a laxative enema, and external and internal stimulants, there was a slight amelioration of the symptoms for about half an hour; but

the collapse again returned, the respiration became slow and difficult, the muscles of the head and trunk rigid, the surface cold, deglutition impossible, and death supervened suddenly, under full consciousness, two hours after the poison had been taken. (*New York Jour. of Med.*, Nov. 1848, 336.)

In another case, a healthy man ate some greens consisting for the most part of the root of aconite. Almost immediately afterward he complained of a feeling as if he could not draw in his tongue, and various hallucinations of sight. These symptoms were soon succeeded by vomiting, involuntary stools and passage of urine, a peculiar sensation in the extremities, a feeling of pricking in the whole body, and fainting, followed by death. (*Reil's Monograph upon Aconite*, 46.)

The following case of recovery occurred in the practice of Dr. McCready, of New York. A healthy Irishwoman, about twenty-five years of age, swallowed a tablespoonful of a saturated tincture of aconite, mistaking it for brandy. When seen an hour afterward, her countenance was flushed, the pupils dilated, though sensible to light; the pulse frequent, soft, and weak, the beat being sometimes so feeble as to be almost imperceptible. She complained of a feeling of fulness about her limbs, as if they were about to burst, accompanied by a sensation of numbness and pricking over the whole surface; and there were numbness and tingling of the tongue, and a strange sensation about the throat. There was no sickness at the stomach, and the head was perfectly clear. An emetic of zinc sulphate and ipecacuanha was administered, and produced copious vomiting. Half an hour afterward, the pulse was still frequent and feeble, the beats continuing irregular in force. She complained of feeling weak, but in other respects was about the same as when first seen. Three hours later, the dilatation of the pupils had passed away, but the numbness and tingling remained. The next day she was almost in her usual health. (*Amer. Jour. Med. Sci.*, Jan. 1852, 268.)

Period when Fatal.—In fatal poisoning by aconite or any of its preparations, death usually occurs in from two to six hours after the poison has been taken; but considerable variation has been observed in this respect.

In a case communicated to me by Prof. L. McLane Tiffany, of Baltimore, two drachms of the tincture of the root proved fatal to a healthy woman, aged thirty-four years, in forty-five minutes after

the poison was taken. In another case, a lotion containing compound liniment of aconite and belladonna, swallowed by mistake, caused the death of a man, under most violent symptoms of aconite poisoning, in about thirty minutes. (*British Med. Jour.*, 1882, i. 774.)

A case is also reported in which one drachm of the tincture, taken by an adult, proved fatal in one hour and a half, the patient being strongly convulsed just before death. In another instance, a child, aged two years and seven months, having eaten an unknown quantity of the fresh leaves of aconite, was soon seized with violent symptoms, but death did not occur until after the lapse of about twenty hours. (*Lancet*, London, June, 1856, 715.) In this case, shortly after the symptoms manifested themselves there was violent vomiting, which brought away pieces of the leaves: no vegetable matter was found in the stomach after death.

In a series of six fatal cases of aconite poisoning communicated to me by Prof. J. W. Mallet, which occurred in the Western Lunatic Asylum of Virginia, in 1883, death took place respectively within *eight minutes, ten minutes, thirteen to fifteen minutes, one hour and a quarter, two hours and a quarter,* and in *four days* after the poison had been taken. Two other patients that had taken the poison fully recovered. The poison, either in the form of the alkaloid or of a very concentrated solution of aconite, had been, in some manner not ascertained, introduced into the several medicines given to these patients. Prof. Mallet readily detected aconitine in the contents of the stomach of three of the patients, and also, in one instance, in the dregs of the medicine administered: these were the only chemical examinations made in these cases.

Fatal Quantity.—Since the preparations of aconite are subject to great variation in strength, similar quantities of the same form of preparation have given rise to very different results. Thus, Dr. Fleming mentions an instance where two grains of the alcoholic extract occasioned alarming effects, and another in which four grains proved fatal; whilst Dr. Christison relates an instance in which he gave six grains of a carefully prepared alcoholic extract to a woman suffering from rheumatism, without being able to observe any effect whatever. (*On Poisons*, 667.) In a case reported by Dr. Easton, twenty-five minims of a tincture of the root of aconite, with twenty minims of tincture of belladonna, caused the death of a healthy young man within three hours; and in another instance twenty-five

drops of the tincture, prescribed through ignorance, proved fatal to a man in about four hours. (*American Medical Monthly*, March, 1854, 223.) Several instances are reported in which about a drachm of the tincture destroyed life.

In a case communicated to Dr. Pereira, two doses of six drops each of the tincture, taken at an interval of two hours, by a young man aged twenty-one years, produced most alarming symptoms. (*Mat. Med.*, ii. 1091.) We are acquainted with an instance in which a very intelligent physician administered to his wife a dose of five drops of Thayer's fluid extract of the root of aconite. In from ten to fifteen minutes afterward she experienced a burning sensation in the throat and great numbness in the arms; these effects were soon followed by tingling in the surface of the whole body, difficulty of breathing, impending suffocation, dimness of vision, and alarming prostration, which continued for about two hours: she then rapidly recovered.

Recovery has not unfrequently taken place after comparatively large quantities of some of the preparations of aconite were taken. In a case reported by Mr. Kay, a lady took by mistake two teaspoonfuls of the tincture, and entirely recovered in eight hours afterward. In this case the symptoms did not manifest themselves until an hour after the poison had been taken. An emetic was then given, which quickly operated. The patient then lost the use of her lower extremities; the face had an anxious expression; the forehead was wrinkled and corrugated; the pupils slightly dilated; pulse slow, feeble, and intermitting; the extremities cold, but the intellect quite unaffected. She complained of a burning sensation in the throat and a constriction at the chest; and lost the sense of feeling in her legs, arms, and face. (*Lancet*, Reprint, Oct. 1861, 273.) In another case, related by M. Devay, a porter in a druggist's shop swallowed by mistake nearly one ounce and a half of an alcoholic solution of aconite, and although he immediately experienced a sense of heat and constriction in the throat and was soon seized with the most violent symptoms, yet he was quite well three days afterward. (*Chemical Gazette*, ii. 220.)

Aconitine in its pure state, as already mentioned, is one of the most virulent poisons known. Dr. Headland considers that one-tenth of a grain of the pure alkaloid would be sufficient to destroy the life of a healthy adult man. And Dr. Pereira mentions an

instance in which one-fiftieth of a grain nearly proved fatal to an elderly lady. (*Mat. Med.*, ii. 1093.) A most remarkable instance of recovery, in which a gentleman had taken two grains and a half of aconitine, is related by Dr. Golding Bird. It seems that almost immediately after taking the poison the patient fell, and was seized with violent vomiting, by which it is believed that most of the poison was ejected. Some time after the occurrence, the patient was in a most fearful state of collapse; the surface cold and perspiring; the action of the heart scarcely perceptible, but the intellect was unimpaired. The most prominent symptom, which continued for some hours, was repeated and most violent convulsive vomiting. On attempting to swallow any fluid the patient was seized with violent spasms of the throat, somewhat similar to those observed in hydrophobia. This latter symptom continued for several hours, and it was not until about thirty hours after the poison had been taken that the patient was considered convalescent. (*New York Journal of Medicine*, March, 1848, 285.)

Three cases of poisoning by aconitine nitrate, one of them fatal, are reported by Dr. A. Busscher. (*Berl. Klin. Wochenschr.*, June, 1880, 337.) In one of these, a feeble man, aged sixty-one years, suffering from chronic bronchitis, took, at the advice of a physician, five drops of a solution containing about 1–165th grain (0.4 milligramme) of the nitrate. The patient immediately experienced a feeling of constriction and burning in the mouth, extending to the stomach; he then felt cold, and laid himself upon a bed. Two hours later, he took twenty drops of the solution, and this dose was repeated except the last, which contained only ten drops, so that during a period of about two days he took in all seven doses, equivalent to about 1–7th grain (9.2 milligrammes) of the nitrate. After each dose he experienced violent symptoms of aconite poisoning, so that at one time it was believed he would certainly die; but he finally recovered.

Dr. Carl Meyer, who prescribed the medicine in the foregoing case, swallowed from fifty to sixty drops of the same solution, equal to about 1–16th grain (4 milligrammes) of the aconite salt. At the end of fifteen minutes symptoms of poisoning began to manifest themselves. About four hours later, his face was pale, the pulse small and irregular, skin cold, pupils contracted, and there was a sense of burning in the mouth, with constriction of the throat, extending to the abdomen. He complained of precordial distress,

and a sense of heaviness and feebleness in the extremities, especially in the legs. The pupils suddenly dilated, and sight was lost, but again returned when the pupils became contracted. Irritation of the pharynx induced vomiting. Convulsions now appeared, attended with congestion of the head, and labored, stertorous respiration. He complained of deafness and ringing, first in one and then in the other ear. After a subcutaneous injection of ether the pupils again dilated, and vision was lost; vomiting again came on, and was followed by violent and prolonged convulsions. He then became unconscious, the pupils insensible to light, the respiration labored, and the heart gradually failing, death took place five hours after the ingestion of the poison. (*Ann. d'Hyg.*, Jan. 1882, 87.)

In these cases, as also in a third, which did not prove fatal, Petit's crystallized aconitine nitrate was taken; whereas Dr. Meyer intended that Friedländer's preparation should be administered, the former being, according to Plugge, 170 times more active than the latter.

In a remarkable case tried in England in 1882, in which George Lamson, a medical practitioner, was convicted of the murder of his brother-in-law, Percy Malcolm John, by the administration of perhaps two grains of aconitine enclosed in a gelatine capsule, the following symptoms were present, as reported by Dr. Thos. Stevenson. (*Guy's Hosp. Rep.*, 1883, 307.) Half an hour after taking the capsule Percy complained of heart-burn, and a little later said that he felt as he had felt on a former occasion when Lamson had given him a quinine pill. After this he complained that his skin felt all drawn up, and that his mouth was very painful. Violent vomiting ensued, and he threw himself about most violently; there was great pain in the region of the stomach, and a sense of constriction in the throat, with inability to swallow. He was so restless and violent that it required great force to restrain him. The pain was incessant till near the time of his death. Finally he became unconscious, his breathing became slower and sighing, the heart's action weaker, and he died four hours and five minutes after taking the capsule.

In another case, quoted by Dr. Stevenson (*Ibid.*), a chemist with suicidal intent took eight grains of Merck's aconitine. In half an hour violent symptoms appeared, and death took place twelve hours after the poison had been taken.

TREATMENT.—In poisoning by aconite or its active alkaloid, the

first indication is to evacuate thoroughly the contents of the stomach, either by an emetic or the use of the stomach-pump. As an emetic zinc sulphate is usually preferred. Stimulants, such as ammonia and brandy, may often be employed with great advantage; and the use of stimulating injections has been attended with good results. As an antidote, the free administration of finely-powdered animal charcoal, mixed with water, has been strongly recommended by Dr. Headland and others. It is claimed that this substance will unite with the poisonous alkaloid, and thus prevent its absorption into the system. The charcoal is then removed from the stomach by an emetic. Vegetable infusions containing tannic acid, and also a solution of iodine in potassium iodide, have been strongly advised, on the ground that they form insoluble compounds with the alkaloid.

From the apparent antagonism existing between the physiological effects of aconite and those of nux vomica, these substances have been recommended as mutual antidotes. The following case, in which this remedy was employed, is reported by Dr. Hanson. A boy, aged five years, swallowed a mixture of tincture of aconite and simple syrup. When first seen by Dr. Hanson, the patient was laboring under the usual symptoms of aconite poisoning, in an aggravated degree. Emetics and tickling the fauces with a feather were resorted to, but without producing vomiting, and the patient continued to sink. Half an hour after the first dose of tartar emetic had been given, three drops of the tincture of nux vomica were administered. In a few minutes the action of the heart was increased in force, and the respiration much improved. At the end of twenty minutes, the dose of nux vomica was repeated. Vigorous vomiting now soon ensued, after which the patient rapidly recovered. (*Amer. Jour. Med. Sci.*, Jan. 1862, 285.)

As a remedy in poisoning by aconite, Dr. J. M. Fothergill advised the use of *digitalis*. And in a case reported by Dr. W. Dobie (*British Med. Jour.*, Dec. 1872, 682), in which the patient had taken an ounce of Fleming's tincture of aconite, a subcutaneous injection of twenty minims of tincture of digitalis was administered. At the end of twenty minutes the patient began to rally, and was soon able to swallow a teaspoonful of the tincture mixed with ammonia and brandy. This mixture was twice repeated within an hour, and the patient rapidly recovered. Dr. P. Hooper has recently reported (*Med. Times*, Feb. 1883, 328) two cases of accidental aconite poison-

ing in which he employed repeated drachm doses of tincture of digitalis with great advantage.

Post-mortem Appearances.—The most common morbid appearances, in death from aconite, are an injected condition of the blood-vessels of the brain and of its membranes, and congestion of the lungs and liver, with more or less redness of the mucous membrane of the stomach and intestines. The stomach and small intestines are frequently found empty. The right cavities of the heart usually contain more or less blood; the blood throughout the body is generally fluid and of a dark color. It need hardly be remarked that none of these appearances are peculiar to death from this substance. In two cases of fatal poisoning by a tincture of the root of aconite, quoted by Dr. Beck, the only morbid appearances observed on dissection were great redness of the lining membrane of the stomach and small intestines.

In an instance quoted by Orfila (*Toxicologie*, ii. 443), in which five persons swallowed each a glass of brandy in which the root of aconite had been macerated, and three of them died, death taking place in about two hours, the following appearances were observed. The œsophagus, stomach, and intestines were found much inflamed, and the blood-vessels, especially the veins, of the digestive tube much injected. The mesentery was also inflamed. The cavity of the peritoneum contained a large quantity of yellowish serum. The lungs were dense, of a bluish and violet hue, slightly crepitant, and gorged with blood. The pericardium contained a large quantity of serum; the heart and large vessels presented nothing remarkable. The brain was healthy, but its blood-vessels somewhat injected.

In the case of the child, already cited, in which the leaves of aconite had been eaten and life was prolonged for about twenty hours, the body presented the following appearances sixty hours after death. The abdomen externally was much discolored; and patchy discolorations were visible on the thighs and legs, but the spots were not so apparent as during life. The stomach was highly inflamed throughout its whole extent; it contained a little fluid of a lightish-brown color, but no food, nor any traces of leaves or other vegetable matter. Various parts of the small intestines presented patches of intense inflammation, in some places approaching to gangrene. The large intestines presented nothing particular. The bladder was full of urine; the spleen somewhat congested. The peri-

cardium contained about half an ounce of bloody serum. The heart was full of uncoagulated blood, and the blood throughout the body was thin and fluid. The other parts of the body were nearly or altogether normal.

In the case of Dr. Meyer, who had taken the nitrate of *aconitine*, there was found great paleness of the body, and the pupils were somewhat dilated. The stomach, lungs, and especially the small intestines, were much congested; but the colon and rectum were pale, as was also the bladder. The heart was dilated, and the right side contained a little liquid blood. The vessels of the membranes of the brain were distended, and at certain points exudations under the arachnoid were present; the ventricles contained a bloody serous effusion, and there was a bloody exudation on the choroid plexus. The blood throughout the body was liquid and of a bright cherry-red color.

In the *Lamson case*, sixty-four hours after death, the pupils were dilated, and the lips pale, as was also the tongue. The membranes of the brain and the brain itself were slightly congested. The lungs, liver, spleen, and kidneys were more or less congested. The heart was very flaccid, and its cavities almost empty. The mucous membrane of the stomach was congested throughout, and presented in places small, slightly raised, yellowish-gray patches. The stomach contained three or four ounces of fluid. The first portion of the duodenum was greatly congested, and patches of congestion were present in other parts of the small intestine. The bladder contained three or four fluid-ounces of urine. (*Guy's Hosp. Rep.*, xxvi. 312.)

Chemical Properties.

In the Solid State.—*Aconitine*, in its pure state, is a transparent, odorless solid, which crystallizes with difficulty, forming either colorless rhombic or hexagonal tables, or small four-sided prisms. It has an acrid taste, followed by a sense of tingling and numbness of the tongue; applied in the form of solution to the skin, it causes a persistent feeling of heat and numbness. These effects are produced by even extremely minute quantities of the alkaloid. Applied in the form of ointment to the eye, it causes much the same effects, with, according to Dr. Pereira, contraction of the pupil. Aconitine is unchanged by exposure to the air. When moderately heated in a tube, it fuses to a transparent liquid, which,

as the heat is increased, becomes brown, then black, and is finally reduced to a solid carbonaceous mass. Heated in the air on a piece of porcelain, it undergoes a similar change, and leaves a black cinder, which is but slowly consumed. According to Dr. Guy, aconitine melts at 60° C. (140° F.), and at 204.4° C. (400° F.) yields sublimates which are amorphous.

As found in the shops, aconitine is usually amorphous and more or less colored, and very variable in strength, some of the samples being almost wholly inert. Dr. Pereira states that he met with a French preparation of which he took one grain without perceiving the least effect either on the tongue or otherwise. And of three samples prepared by different German manufacturers that we have examined, one contained only a mere trace of the alkaloid, and the other two appeared to consist entirely of foreign matter. The aconitine prepared by Mr. Morson is usually in the form of a dull white powder, consisting chiefly of small granules and thin, transparent plates. This manufacturer, Mr. Groves, and others, have obtained the alkaloid in the form of large, well-defined crystals. A sample of Duquesnel's aconitine in our possession is in the form of large, colorless crystals, many of them weighing about 1–10th grain each.

Aconitine has strongly basic properties, completely neutralizing acids to form salts, several of which have been obtained in the crystalline form. When touched in the dry state with concentrated *sulphuric acid*, *pure aconitine* slowly dissolves, without any coloration whatever, to a colorless solution, which remains unchanged for many hours. A small crystal of potassium nitrate stirred in a sulphuric acid solution of the alkaloid produces no visible change, even on the application of a moderate heat; if a crystal of potassium dichromate be stirred in the solution, the mixture slowly acquires a green color, due to the separation of chromium sesquioxide. Concentrated *nitric acid* dissolves the alkaloid to a colorless solution, which is unchanged by a moderate heat, and by a solution of stannous chloride. The alkaloid is also dissolved to a colorless solution by hydrochloric acid.

Solubility.—When excess of Morson's aconitine is kept in contact with *pure water* at a temperature of about 15.5° C. (60° F.) for ten hours, one part dissolves in 1783 parts of the fluid. On evaporating the solution to dryness, the alkaloid is left in the form of a hard,

transparent, colorless, vitreous mass, which, when broken up, presents the appearance of crystalline plates. The recently precipitated alkaloid is much more soluble in water than just stated. A sample of Duquesnel's crystallized aconitine had about the same degree of solubility in water as that of Morson. *Absolute ether* kept in contact with excess of aconitine for several hours, at the ordinary temperature, takes up one part in 777 parts of the menstruum. On allowing the solution to evaporate spontaneously, the alkaloid is left as a transparent glacial mass. *Chloroform* readily dissolves the alkaloid in nearly every proportion, and leaves it on spontaneous evaporation in the form of a vitreous mass. It is also freely soluble in alcohol. The *salts* of aconitine are, with few exceptions, readily soluble in water. They are also soluble in alcohol, but insoluble in ether.

Of Solutions of Aconitine.—In the following investigations in regard to the behavior of solutions of aconitine, pure aqueous solutions of the hydrochloride were employed. The fractions indicate the fractional part of a grain of the pure alkaloid present in one grain of liquid; and, unless otherwise stated, the results refer to the behavior of one grain of the solution.

1. *The Caustic Alkalies.*

The fixed caustic alkalies and ammonia throw down from somewhat concentrated solutions of salts of aconitine a dirty-white, flocculent precipitate of the hydrate of the alkaloid, which is nearly wholly insoluble in excess of the precipitant, but readily soluble in free acids, even acetic acid.

1. $\frac{1}{100}$ grain of aconitine, in one grain of water, yields a rather copious precipitate, which is insoluble in large excess of the reagent.
2. $\frac{1}{500}$ grain yields a quite good precipitate, which dissolves, not readily, however, in several drops of the precipitant.
3. $\frac{1}{1000}$ grain: no satisfactory indication.

The *alkali carbonates* fail to produce a precipitate with a 1–100th solution of the alkaloid.

2. *Auric Chloride.*

Trichloride of gold produces in solutions of salts of aconitine, even when highly diluted, a yellow, amorphous precipitate, consisting

of aconitine hydrochloride and auric chloride, which is but very sparingly soluble in hydrochloric acid.

1. $\frac{1}{100}$ grain of aconitine yields a very copious precipitate.
2. $\frac{1}{1000}$ grain yields a quite good deposit, which is readily soluble to a clear solution in potassium hydrate.
3. $\frac{1}{5000}$ grain yields in a very little time a quite fair precipitate.
4. $\frac{1}{10,000}$ grain yields after a little time a quite perceptible deposit.
5. $\frac{1}{20,000}$ grain: after some time a just perceptible turbidity.

3. *Picric Acid.*

An alcoholic solution of picric acid occasions in solutions of salts of aconitine a yellow, amorphous precipitate, which is insoluble in ammonia.

1. $\frac{1}{100}$ grain of aconitine, in one grain of water, yields a very copious precipitate.
2. $\frac{1}{1000}$ grain yields a quite fair, greenish-yellow deposit.
3. $\frac{1}{5000}$ grain: after a little time a quite perceptible precipitate.

4. *Iodine in Potassium Iodide.*

An aqueous solution of iodine in potassium iodide throws down from solutions of aconitine and of its salts, even when highly diluted, a reddish-brown or yellowish, amorphous precipitate, which is readily decomposed by the caustic alkalies.

1. $\frac{1}{100}$ grain of aconitine yields a very copious precipitate, which on the addition of potassium hydrate is changed to a white deposit.
2. $\frac{1}{1000}$ grain: a copious, yellowish precipitate, which is soluble in the caustic alkalies, but immediately replaced by a white deposit.
3. $\frac{1}{10,000}$ grain: a quite good precipitate.
4. $\frac{1}{50,000}$ grain yields a quite distinct deposit.
5. $\frac{1}{100,000}$ grain: the mixture becomes distinctly turbid.

5. *Bromine in Bromohydric Acid.*

A strong aqueous solution of bromohydric acid saturated with bromine produces in solutions of salts of aconitine, and of the free alkaloid, a yellow, flocculent precipitate.

1. $\frac{1}{100}$ grain of aconitine, in one grain of water, yields a copious precipitate.
2. $\frac{1}{1000}$ grain: a quite good deposit.

3. $\frac{1}{10,000}$ grain: a quite fair precipitate.
4. $\frac{1}{25,000}$ grain yields a distinct cloudiness.

Other Reagents.—*Corrosive sublimate* produces in one grain of a 1–100th solution of salts of aconitine a quite good, dirty-white, caseous precipitate, which is readily soluble in hydrochloric acid. A similar quantity of a 1–500th solution of the alkaloid fails to yield a precipitate. *Potassium sulphocyanide* and *tannic acid* produce a perceptible cloudiness in a 1–100th solution of salts of the alkaloid. With stronger solutions these reagents produce distinct precipitates. *Phospho-molybdic acid* throws down a precipitate from solutions of the alkaloid even when highly diluted.

Platinic chloride, potassium chromates, potassium iodide, and potassium ferro- and ferri-cyanide, fail to produce a precipitate with a 1–100th solution of the hydrochloride of the alkaloid.

Fallacies.—None of the chemical reactions now described are in themselves characteristic of aconitine, they being common to many of the alkaloids and certain other organic principles; nor is there at present any chemical reaction known that in itself is peculiar to this substance. By, however, the concurrent reaction of several of these reagents, taken in connection with the peculiar effects of the alkaloid upon the tongue, its nature may be fully established, even when present only in very minute quantity. In fact, the symptoms produced by this substance are usually so peculiar that they alone, when fully known, may enable the medical jurist to determine the cause of death, even when the chemical evidence has entirely failed. A case of this kind, in which the root of aconitine had been criminally administered and no trace of the poison was discovered in the body, is related by Dr. Geoghegan. (*Dublin Medical Journal*, July, 1841, 403.)

Physiological Test.—Much the most characteristic test yet known for the recognition of aconitine is its peculiar physiological action when applied to the tongue or in the form of solution to the skin. A drop of water holding in solution, in the form of a salt, only the 1–1000th of a grain of the alkaloid, when placed upon the end of the tongue, causes, as first observed by Dr. Headland, a very decided tingling and numbness of that organ, which continue for an hour or longer. According to Dr. Headland (*Action of Medicines*, 448), the 1–100th of a grain dissolved in alcohol and rubbed into the skin

produces loss of feeling, lasting for some time; and the 1–50th of a grain will kill a small bird almost instantly.

In an experiment by Dr. T. Stevenson, 1–3000th grain of Morson's crystallized aconitine, subcutaneously injected, killed a large mouse in eighteen minutes. And our own experiments with Duquesnel's crystallized aconitine indicated it to be about equally potent, 1–3000th grain proving fatal to a mouse, under violent retching followed by convulsions, in thirty-two minutes. A sample of Morson's ordinary aconitine was somewhat less active than the crystallized alkaloid of Duquesnel; as was also a sample of Trommsdorff's aconitine, which latter was in the form of a faintly colored, partially granular powder.

Separation from Organic Mixtures.

Suspected Solutions and Contents of the Stomach.—In suspected poisoning by *aconite* in its crude state, before proceeding to a chemical examination of the mixture presented for examination, the analyst should carefully examine it for any solid portions of the plant, which, if found, may be identified by their botanical characters. All parts of the plant have a bitter taste, which is soon followed by a persistent sense of numbness and tingling in the lips and tongue.

Aconitine may be separated from the contents of the stomach, and like mixtures, in the same manner as heretofore described for the recovery of nicotine (*ante*, 447), or by the method of Stas. The alkaloid is more readily extracted from aqueous mixtures by chloroform than by ether, it being much more soluble in the former than in the latter liquid. The residue obtained on evaporating the chloroform or ether extract should at first be stirred with a few drops of water containing a trace of acetic acid, and a small portion of the mixture applied to the end of the tongue. If this experiment indicates the presence of a very notable quantity of the poison, the remaining portion of the mixture may be dissolved in an appropriate quantity of acidulated water and the solution examined by some of the chemical tests. Should, however, the portion applied to the tongue fail to indicate the presence of the alkaloid, another and larger portion should be examined in the same manner, even if the whole of the mixture be thus consumed, since without the corrobora-

tion of this physiological test, the chemical tests, at present known, would be of no avail.

On applying the method heretofore pointed out for the detection of nicotine to the examination of the contents of the stomach of a dog, killed in fourteen minutes by a drachm of ordinary tincture of the root of aconite, the presence of aconite was very fully established.

From the Blood.—Absorbed aconitine may be recovered from the blood by slightly acidulating the fluid with sulphuric acid and agitating it in a wide-mouthed bottle with something more than its own volume of diluted alcohol, until the mixture becomes homogeneous. It is then placed in an evaporating-dish and exposed for some time, with frequent stirring, to a moderate heat; the cooled mass is transferred to a moistened linen strainer, and the solids retained by the strainer well washed with diluted alcohol and strongly pressed. The liquid is now concentrated at a moderate heat, again strained, then evaporated to a small bulk, filtered through paper, and evaporated on a water-bath to about dryness. The residue thus obtained is well stirred with a small quantity of pure water, the solution filtered, then rendered alkaline, and thoroughly agitated with about two volumes of chloroform, which, after separation and decantation, is allowed to evaporate spontaneously, when the alkaloid will usually be left sufficiently pure for testing.

About forty minims of the tincture of aconite root were administered to a small dog. The animal immediately indicated an uneasy sensation in the mouth and throat, and soon vomited a white frothy mucus, then lost the use of his legs, made repeated attempts to vomit, had spasmodic convulsions with slow breathing, and died in sixty-four minutes after the dose had been given. Twelve fluid-drachms of blood, taken immediately from the animal, were submitted to the foregoing method of analysis, and the chloroform residue stirred with two drops of water containing the merest trace of acetic acid. A drop of this mixture placed upon the tongue gave, in a little time, perfectly unequivocal evidence of the presence of aconitine. The remaining drop of the mixture was diluted with two drops of pure water, and examined in three separate portions by picric acid, auric chloride, and a solution of bromine, all of which produced precipitates very similar in quantity with those produced from a 1–1500th solution of the alkaloid. The entire quantity of the poison recovered could hardly have exceeded the 1–300th of a grain, and may have

been even much less than this, since it is by no means certain that the precipitates produced by the reagents were perfectly pure.

Twenty-five minims of the same tincture of aconite were given to a healthy cat. The animal was soon seized with violent vomiting, lost the power of walking, frothed at the mouth and nose, and died under violent symptoms within thirty minutes. The chloroform residue obtained from one ounce of blood from this animal, when stirred with a few drops of acidulated water and examined by auric chloride and a solution of bromine, gave reactions similar to those produced from a quite dilute solution of aconitine; yet about one-half of the residue, when applied to the tongue, failed to produce any decided effect upon that organ.

In the *Lamson case*, Drs. Stevenson and Dupré found aconitine in extracts from the viscera, the vomit, and the urine of the victim, the presence of the alkaloid being determined by the general chemical nature of the extract, its effect upon the tongue, and its action upon mice.

The general method of analysis followed in this case was to repeatedly extract the substance with alcohol slightly acidulated with tartaric acid, and then evaporate the filtered alcoholic extract to dryness at 35° C. (95° F.). The residue thus obtained was exhausted with tepid water, and the filtered liquid, while still acid, repeatedly agitated with ether. The aqueous liquid was then rendered alkaline by sodium carbonate, and extracted with a mixture of ether and chloroform; the ethereal mixture was evaporated to dryness, and the residue examined for aconitine.

Section II.—Atropine. Belladonna.

History.—Atropine is the active principle, or alkaloid, of *Atropa Belladonna*, or *Deadly Nightshade*. It exists in the root, leaves, and berries of the plant. The existence of this principle was first announced in 1819, by Brandes; but it was first obtained in its pure state by Mein, a German pharmaceutist, in 1833. Its composition, according to the analyses of Planta, is $C_{17}H_{23}NO_3$. Atropine is a white crystallizable solid, and a most virulent poison.

Preparation.—Atropine may be obtained, according to M. Rabourdin, in the following manner. The fresh leaves of the plant are

well bruised and submitted to pressure to extract the juice; this is then heated to about 85° C. (185° F.), in order to coagulate the albumen, and filtered, after which it is rendered alkaline by potassium hydrate, and thoroughly agitated for a few minutes with *chloroform*. In about half an hour, the latter fluid, holding in solution the atropine and having the appearance of a greenish oil, will have subsided to the bottom of the mixture. The supernatant liquid is then decanted, and the chloroform solution washed with successive portions of water as long as this liquid becomes colored. The chloroform solution is then transferred to a tubulated retort, and distilled in a water-bath until all the chloroform has passed into the receiver, when the residue is treated with a little water acidulated with sulphuric acid, which will dissolve the atropine, leaving a green, resinous matter. The solution thus obtained is filtered, the filtrate treated with slight excess of potassium carbonate, and the precipitated atropine collected on a filter, washed, and dissolved in rectified alcohol, which upon spontaneous evaporation will leave the alkaloid in beautiful groups of acicular crystals.

In the absence of the fresh plant, M. Rabourdin recommends to employ the extract of belladonna. Thirty parts of the extract are dissolved in one hundred parts of water, and the filtered solution agitated for about a minute with two parts of potassium hydrate and fifteen parts of chloroform. The subsequent steps of the process are the same as directed above, except that the washed chloroform solution, instead of being distilled, is allowed to evaporate spontaneously. The product obtained by either of these methods, if not perfectly colorless, may be further purified, as first advised by Prof. Procter, by redissolving it in water acidulated with sulphuric acid and extracting the foreign organic matter by chloroform; the aqueous solution is then rendered alkaline, and the liberated alkaloid extracted with fresh chloroform, which on spontaneous evaporation will leave it in its pure state. M. Lefort has advised the use of *ether*, instead of chloroform, for the extraction of the alkaloid, the latter being first extracted from the leaves of the plant by boiling water containing one per cent. of tartaric acid.

Mein, in his experiments, obtained twenty grains of atropine from twelve ounces of the fresh root of belladonna; and Luxton, between five and six grains from one thousand grains of the fresh leaves. On an average, perhaps, the green root and leaves do not contain over

about one-third of one per cent. of the alkaloid. According to M. Lefort, the proportion of atropine in belladonna root varies very greatly according to the age of the plant, young roots being richer in the alkaloid than the roots of plants more than two or three years old.

The ordinary medicinal dose of *atropine*, and its *salts*, is about one-fiftieth of a grain. The pharmaceutical *extracts* and *tincture* of belladonna are each subject to great variation in strength. The dose of the former, for an adult, is at first from one-fourth to one-half a grain; that of the latter, from fifteen to twenty-five minims.

Poisoning by atropine in its pure state has been of rather rare occurrence; but numerous instances of poisoning by the berries and some of the preparations of belladonna are recorded. With few exceptions, however, these cases have been the result of accident, most of them having been occasioned by the berries being eaten through ignorance of their properties. The berries have considerable resemblance to cherries, and a sweet but mawkish taste.

Symptoms.—The most constant symptoms occasioned by poisonous doses of belladonna are dryness of the mouth and throat, difficulty of deglutition, dilatation of the pupils, impaired vision, and delirium, succeeded by drowsiness and stupor. The delirium is generally of a pleasing character, but sometimes of a furious nature. These effects are usually attended with a sense of burning and constriction of the throat, impaired articulation, great thirst, giddiness, numbness of the limbs, a staggering gait, nausea and sometimes vomiting, spectral illusions, and great mental excitement. The pulse becomes quick and small, and sometimes the face red and turgid, and the eyes wholly insensible to light. The secretions are usually increased; irritation of the urinary organs has sometimes occurred; and in some instances a scarlet eruption has appeared on the skin. In fatal cases, death is usually preceded by coldness of the extremities, a rapid and intermittent pulse, deep coma, and sometimes, though rarely, convulsions.

The following symptoms were observed in one hundred and fifty French soldiers, who had eaten the berries of the plant: Dilatation and immobility of the pupil, with total insensibility of the eye to the presence of external objects, or at least confused vision; bluish injection of the conjunctiva; great prominence of the eye; dryness of the lips, tongue, and throat; difficult and in some cases impossi-

ble deglutition; nausea, but no vomiting; great weakness, with difficulty or impossibility of standing; continual movement of the hands and fingers; lively delirium, accompanied with a silly laugh; aphonia, or confused sounds uttered with difficulty; and ineffectual attempts to empty the bowels. These effects were followed by very gradual return to health and reason, without any recollection of the preceding state. (*Orfila's Toxicologie*, 1852, ii. 478.)

The symptoms produced by belladonna, as usually developed, could not readily be confounded with those of any other substance, except stramonium and hyoscyamus (Pereira). The symptoms usually manifest themselves within an hour after the poison has been taken; but they have frequently been delayed for several hours, especially in poisoning by the berries. Of the numerous recorded cases of poisoning by this substance, comparatively few proved fatal, and in these the time of death varied from a few hours to some days. The effects in non-fatal cases are frequently very slow in disappearing, sometimes lasting for several days or even weeks.

A healthy man ate of a pie made with the *berries* of belladonna and apples. A few minutes after taking his dinner he complained of feeling drowsy; the lethargy soon increased, his countenance changed color, the pupils became dilated, and he experienced a strange coppery taste in his mouth. On going up-stairs, he staggered, and, upon entering his room, fell, and became insensible. He subsequently became delirious and convulsed, and died the following morning. A child to whom a portion of the pie had been given died on the same day. (*New York Jour. of Med.*, viii. 284.) In another case, in which a child had eaten the berries of the plant, narcotic symptoms appeared in two hours, and death took place in nineteen hours, being preceded by coma and a temperature of 43.3° C. (110° F.) for several hours before the fatal result. (*Med. Times*, Nov. 1882, 94.)

In four cases in which some boys had eaten a quantity of the *extract* of belladonna, in one instance as much as a drachm, the following symptoms were observed in one of the cases. When first seen by a physician, the patient was quite delirious, the delirium being of a fantastic character; he could neither hear nor speak plainly, and labored under hallucinations, but was otherwise unconscious. The pupils were widely dilated, and the eyes had a staring

look. At first he complained of some pain in the throat and of his imperfect sight, objects appearing white to him. The pulse was very feeble, and almost countless; and there was great difficulty of swallowing. Under active treatment, including the use of an emetic, the delirium, having lasted eighteen hours, gradually passed away; but it was not until the lapse of forty hours that he was perfectly rational. Much the same symptoms were present in the three other cases. All the patients finally recovered. (*Lancet*, 1860, i. 133.)

Dr. Hibbert Taylor reports a case (*British Med. Jour.*, Nov. 1869, 555) in which a youth, aged sixteen years, swallowed by mistake about a drachm of the *extract*, and died from its effects three hours and three-quarters thereafter. In this instance, violent symptoms suddenly manifested themselves about an hour after the extract had been taken. About an hour before death the patient became comatose, and so continued until he died.

The following instance of recovery is related by Dr. H. M. Gray. (*New York Jour. of Med.*, Sept. 1845, 182.) A child, between two and three years of age, swallowed from eight to twelve grains of the *extract* of belladonna. Something over half an hour after taking the poison, the expression of the patient was that of terror; the pupils were widely dilated and immovable, the conjunctiva highly injected, and the whole eye prominent and very brilliant. The face, upper extremities, and trunk of the body exhibited a diffuse scarlet efflorescence studded with innumerable papillæ, very closely resembling the rash of scarlatina. The skin was hot and dry; the pulse much increased in force and frequency; the respiration anxious, and attended with the stridulous sound of croup. There was also a constant but unsuccessful effort at deglutition, with spasmodic action of the muscles of the throat and pharynx; and paroxysms of violent motion and rapid automatic movements, attended with convulsive laughter. Under the action of an emetic the alarming symptoms passed off in about three hours, and the child soon recovered, with the exception of a moderate diarrhœa and a slight enlargement of the pupil. Dr. Stevenson reports a case (*Guy's Hosp. Rep.*, xiv. 267) in which a child, less than three years of age, recovered after having taken five grains of the extract.

The *external application* of belladonna, and its administration in the form of an *enema*, have in several instances given rise to serious and even fatal results. A case is related in which an injection of a

decoction of the root caused the death of an adult in five hours; and another, in which only two grains of the extract, administered in the same manner, gave rise to alarming symptoms. Dr. Lyman relates an instance in which the application of a small belladonna plaster to the chest of a nervous woman produced all the usual symptoms of poisoning by that substance, from which the patient did not entirely recover until after four or five days. Two cases of this kind, in which a lotion of belladonna had been applied, are mentioned in the *Chemical News* (London, Nov. 1866, 216).

In a case reported by Dr. Smith (*Boston Med. and Surg. Jour.*, Dec. 1879, 895), an application of belladonna ointment to the neck of the womb of a woman in labor was followed in less than fifteen minutes by dizziness, succeeded in quick succession by great thirst, dryness and burning of the mouth and fauces, nausea and ineffectual attempts to vomit, spasmodic movements of the arms, and striking at imaginary objects. There were short intervals of repose, then sudden convulsive movements; the pulse became feeble, the extremities cold, and the pupils widely dilated. Under the subcutaneous injection of a third of a grain of morphine the convulsive movements soon subsided; but the thirst and dryness of the throat remained for ten or twelve hours. Labor-pains did not again appear for ten days, when the woman was safely delivered.

Atropine.—The symptoms produced by *atropine* in its pure state are the same in kind as those occasioned by belladonna, but they are usually much more prompt in appearing. In a case related by Dr. Schmid, a stout, healthy man swallowed from one-sixth to one-fourth of a grain of the alkaloid in solution. An hour afterward, the patient was in a state of fearful excitement; the tongue was swollen and projected between the teeth, and he incessantly moved it and his lips in a stammering manner, but without emitting a single intelligible word. The eyes were staring; the head hot, and the countenance livid; the pupils dilated to their utmost, and insensible to light; the pulse was rapid, full, and strong, and there was a constant desire, but without the power, to make water. During the following hour the excitement continually increased, when the subcutaneous injection of one-fifth of a grain of morphine acetate into the right temple was soon succeeded by a state of calm. After two hours more, the excitement had again attained almost its former height, but it was again subdued by a repetition of the morphine injection. The patient now gradually recovered,

the only symptoms remaining about twenty-four hours after the occurrence being extreme weakness, dryness of the throat, slight twitchings of the limbs, and a dilated state of the pupils. (*Amer. Jour. Med. Sci.*, July, 1866, 269.)

Dr. S. W. Gross reports a case (*Amer. Jour. Med. Sci.*, Oct. 1869, 401) in which a healthy woman, aged forty-three years, through the mistake of a druggist, took some pills containing *three grains* of atropine, and died from the effects of the poison in about fifteen hours after taking the dose. The symptoms in this case began in about fifteen minutes after the pills had been taken, there being at first violent agitation, soon followed by pleasant delirium, in which the patient picked at her clothes, tried to get out of bed, and imagined she was sewing, or nursing her child, or engaged in shopping with her sister.

Dr. Andrew, of Edinburgh, relates an instance in which *two-thirds* of a grain, taken in mistake by a female, produced most violent symptoms, from which the patient did not entirely recover for more than a week. (Wharton and Stillé, *Med. Jur.*, 639.) And in a more recent case, a similar quantity of the sulphate of the alkaloid, taken by a lady, caused most alarming symptoms during a period of eighteen hours, although the contents of the stomach had been early evacuated by means of the stomach-pump. (*Amer. Jour. Pharm.*, July, 1871, 324.) An instance is mentioned in which a solution of only *one-twelfth* of a grain of atropine taken in mistake by a physician caused his death in about thirty hours. (*Gaillard's Med. Jour.*, May, 1880, 583.)

On the other hand, Dr. Roux has reported an instance in which a lady, in a fit of despair, swallowed a solution containing nearly *two grains* of atropine, and entirely recovered, not, however, without suffering the most severe symptoms. The treatment employed in this case consisted of emetics, followed by a strong decoction of coffee and M. Bouchardat's solution of iodine in potassium iodide.

The employment of atropine in the form of *subcutaneous* injection has in repeated instances been followed by very serious and even fatal results, even when injected in very minute quantity. Dr. Eulenberg relates an instance in which he employed in this manner, in the case of a lady affected with facial neuralgia, 1–48th of a grain of the alkaloid, and alarming symptoms of poisoning soon appeared. The patient threw herself about the bed entirely unconscious, and from time to time broke out in furious delirium; the limbs, and also

the head, were shaken with convulsive jerkings. The pupils were moderately dilated, the pulse small, and somewhat increased in frequency. An immediate injection of one-third of a grain of morphine into the temporal region, in close proximity to the former place of injection, was followed within about three minutes by a cessation of the twitchings, and in ten minutes the patient fell into a heavy, peaceful sleep, from which she awoke in eight hours without any symptom of the poison being present. (*Amer. Jour. Med. Sci.*, April, 1866, 434.) In another case, related by Dr. Lorent, less than the 1–100th of a grain of the alkaloid, employed in this manner, produced very alarming results. Dr. Arnold mentions an instance in which death resulted in five minutes from the *one-thirtieth* of a grain of atropine given hypodermically. (*Baltimore Med. Jour.*, March, 1871, 169.) On the other hand, Dr. T. B. Jewett relates a case in which recovery took place after the subcutaneous injection of a solution of *one grain* of atropine, three grains of morphine having been administered hypodermically soon after the atropine had been injected. (*Proc. Connecticut Med. Soc.*, 1879, 82.)

The *external* application of atropine may speedily produce death. In an instance reported by Dr. Ploss, of Leipsic, an ointment composed of fifteen parts of atropine sulphate to seven hundred parts of lard, applied as a dressing to a blistered surface on the neck of a man, caused death, under the most violent symptoms of belladonna poisoning, within two hours after the application had been made. (*Amer. Jour. Med. Sci.*, April, 1865, 541.) A few drops of an aqueous solution containing two-thirds of a grain of the alkaloid to the ounce of fluid, applied to the eye of a man affected with cataract, produced violent constitutional effects, with constant hallucinations, and inability to pass urine; the violent delirium continued during the ensuing night, and it was some days before the patient entirely recovered.

Treatment.—This consists, in case the poison has been swallowed, in the speedy administration of an emetic or the employment of the stomach-pump. Of the various chemical antidotes that have been proposed may be mentioned tannic acid, a solution of iodine in potassium iodide, hydrate of magnesia, and animal charcoal. If either of these substances be employed, it should only be in connection with emetics or the use of the stomach-pump.

As a physiological antidote, *morphine*, administered either by the mouth or by subcutaneous injection, has been found very beneficial,

as in some of the instances already cited. In a case of recovery mentioned by Dr. J. B. Cox, in which one grain of atropine had been taken, it is said that from sixteen to eighteen grains of morphine were injected hypodermically without there being at any time symptoms of narcotism from the use of the morphine. (*Med. Times*, Feb. 1884, 377.)

Pilocarpine, employed subcutaneously, has also been strongly advised in atropine poisoning. Dr. Purjesz relates a case in which about two grains and a half of atropine had been taken, and under the use of repeated injections of a salt of pilocarpine, using in all about 6.4 grains of the salt, the toxic symptoms gradually subsided, and at the end of three hours after taking the atropine the patient had quite recovered, even the dilatation of the pupils having passed off.

Post-mortem Appearances.—These, as in death from most of the vegetable poisons, are subject to considerable variation. The more constant appearances are a dilated state of the pupils, more or less redness of the mucous membrane of the stomach and small intestines, fulness of the cerebral vessels, and congestion of the lungs. The blood is usually dark-colored and liquid. Instances are related, however, in which this poison produced death without leaving any notable morbid change in the body.

In the case reported by Dr. H. Taylor, in which a drachm of the extract of belladonna had been taken, eighteen hours after death, the pupils were found greatly dilated. The lungs were much engorged; and the pleural cavities contained a little dark blood. The heart was empty, except the right auricle, which contained about six drachms of dark, semi-coagulated blood. The stomach was fragile and softened in texture. All the other abdominal organs appeared healthy.

In Dr. Gross's case, in which three grains of atropine had been taken and proved fatal in about fifteen hours, thirty-eight hours after death the pupils were somewhat dilated, and the face was livid. The vessels of the pia mater were turgid with blood, and there was great subarachnoid effusion; the brain-tissue was greatly softened. The lungs were congested; the heart was very soft, and its cavities contained fluid blood. The intestines were pale, but the stomach presented suggillations at its cardiac extremity; the kidneys were congested; and the bladder was empty.

Chemical Properties.

In the Solid State.—*Atropine*, in its pure state, is a white, odorless solid, which crystallizes in the form of transparent prisms, usually aggregated into beautiful tufts or stellated groups. It has a bitter, acrid taste. When heated in a tube, it readily fuses to a colorless, transparent liquid, which ascends the sides of the tube; upon cooling, the liquid becomes a clear gummy mass, and ultimately concretes to a vitreous solid. When gradually heated on porcelain, it fuses and is slowly dissipated, giving rise to dense white fumes. According to Planta, the fusing point of atropine is 90° C. (194° F.), and at 140° (284° F.) it is volatilized, partially unchanged, the greater part undergoing decomposition. When rapidly heated, it melts, puffs up, then evolves dense white fumes, and takes fire, burning with a bright flame, and leaving a shining black cinder, which may be entirely consumed. Heated in contact with a fixed caustic alkali, it readily undergoes decomposition, with the evolution of ammonia.

Atropine has strongly basic properties, and completely neutralizes even the most powerful acids, forming salts, several of which are readily crystallizable. Concentrated *nitric acid* dissolves the pure alkaloid without change of color, even upon the application of heat: the subsequent addition of stannous chloride produces no visible change. So, also, concentrated *sulphuric acid* dissolves it to a colorless solution, which is unchanged by a crystal of potassium nitrate; on the addition of a crystal of potassium bichromate, the acid solution slowly acquires a green color, due to the formation of chromium sesquioxide.

Solubility.—A sample of atropine examined by Planta was soluble in 299 parts of *water* at the ordinary temperature; but a single experiment in our own hands indicated that the alkaloid requires 414 parts of that liquid for solution, even after several hours' digestion. It is readily soluble in nearly every proportion in *alcohol* and in *chloroform*, and is freely soluble in absolute *ether*. Upon spontaneous evaporation, it separates from either of these liquids in the crystalline form. A saturated aqueous solution of the alkaloid has a well-marked alkaline reaction. Most of the *salts* of atropine are freely soluble in water and in alcohol; but they are almost wholly insoluble in ether and chloroform; at least this is the case with the sulphate and hydrochloride.

Of Solutions of Atropine.—The following results, in regard to the behavior of solutions of atropine, are based upon the examination of two apparently perfectly pure specimens of the alkaloid, prepared by different well-known European manufacturers, one of the samples being employed in the form of sulphate, and the other as hydrochloride. The fractions employed indicate the fractional part of a grain of the pure alkaloid present in one grain of water; and the results, unless otherwise indicated, refer to the behavior of one grain of the solution.

1. *The Caustic Alkalies.*

The fixed caustic alkalies throw down from concentrated aqueous solutions of salts of atropine a white, amorphous precipitate of the pure alkaloid, which is readily soluble in free acids, and also in large excess of the precipitant. After a time, especially if the mixture has been stirred, the precipitate assumes the crystalline form. The presence of foreign organic matter readily prevents the formation of crystals.

One grain of a 1–100th solution of the alkaloid yields a quite copious precipitate, which on being stirred with a glass rod becomes in a little time a mass of crystals, of the forms illustrated in Plate XII., fig. 4. Solutions but little more dilute than this fail to yield a precipitate.

Ammonia produces in solutions of salts of the alkaloid the same precipitate as occasioned by the fixed caustic alkalies; but the deposit is much more readily soluble in excess of the precipitant.

Potassium carbonate produces in a 1–100th solution of the alkaloid a distinct turbidity; but the carbonates of sodium and ammonium fail to produce in a similar solution any visible reaction.

2. *Bromine in Bromohydric Acid.*

An aqueous solution of bromohydric acid saturated with free bromine produces in solution of salts of atropine and of the free alkaloid, even when highly diluted, a yellow, amorphous precipitate, which in a little time becomes crystalline. The precipitate from somewhat strong solutions of the alkaloid after a time disappears; but it is immediately reproduced upon further addition of the reagent. The precipitate is insoluble in acetic acid, and only very sparingly soluble in large excess of hydrochloric, nitric, and sulphuric

acids, and in the fixed caustic alkalies: it is even produced from solutions of the alkaloid in concentrated sulphuric acid.

1. $\frac{1}{100}$ grain of atropine, in one grain of water, yields a very copious, bright yellow, amorphous precipitate, which very soon, beginning along the margin, becomes a mass of crystals, Plate XII., fig. 5. After several minutes most of the crystals dissolve, but they may be reproduced, even several times, by further addition of the reagent.
2. $\frac{1}{1000}$ grain yields a copious, yellow deposit, which soon furnishes crystals having the forms illustrated above.
3. $\frac{1}{10,000}$ grain: a quite good, yellowish precipitate, which in a few moments becomes granular and crystalline, and presents the appearance figured in Plate XII., fig. 6.
4. $\frac{1}{25,000}$ grain: in a very little time a quite satisfactory deposit of short crystalline needles and granules.
5. $\frac{1}{50,000}$ grain: after some minutes a few granules appear, but the result is not satisfactory.

The production of the above crystals is quite characteristic of this alkaloid. Although the reagent produces yellow precipitates with most, if not all, of the other alkaloids, and with certain other organic substances, yet all these deposits, with the exception of that from *opianyl*, unlike the atropine precipitate, remain amorphous. The crystallized atropine deposit is readily distinguished from the opianyl compound by its form. It may here be remarked that the reagent produces a similar crystalline precipitate with *daturine*, and also with *hyoscyamine;* but, as we shall see hereafter, there are strong reasons for believing these alkaloids to be identical with atropine. We have found the bromine precipitate to become crystalline in the presence of even comparatively large quantities of foreign organic matter. In the absence of a solution of bromohydric acid, an alcoholic solution of bromine may be employed as the reagent.

3. *Picric Acid.*

An alcoholic solution of picric acid occasions in somewhat strong solutions of salts of atropine a yellow, amorphous precipitate, which is readily soluble in acids, even in acetic acid. After a time the precipitate becomes more or less crystalline.

1. $\frac{1}{100}$ grain of atropine yields a copious, light yellow deposit. If the mixture be stirred with a glass rod, it soon yields streaks of

granules along the path of the rod, and in a little time the deposit becomes entirely crystalline, the crystals being principally in the form of transparent plates, and these more or less aggregated into very beautiful groups, Plate XIII., fig. 1.

2. $\frac{1}{1000}$ grain: within a few moments a slight, greenish-yellow precipitate appears, and in a little time there is a quite good deposit. If the mixture be stirred, it soon yields a fine crystalline deposit.

3. $\frac{1}{5000}$ grain: upon stirring the mixture, it yields after a little time caseous streaks over the bottom of the watch-glass containing the mixture; but the reaction is not very satisfactory.

This reagent also produces crystalline precipitates with various other substances, but the forms illustrated above are quite peculiar to atropine.

4. *Auric Chloride.*

This reagent produces in solutions of salts of atropine, when not too dilute, a light yellow, amorphous precipitate of *atropine chloroaurate*, $C_{17}H_{23}NO_3,HCl,AuCl_3$, which after a time becomes converted into crystals. The precipitate is insoluble in potassium hydrate, and but sparingly soluble in acetic and hydrochloric acids.

1. $\frac{1}{100}$ grain of atropine yields a copious precipitate, which soon becomes a mass of crystals having the peculiar forms shown in Plate XIII., fig. 2.

2. $\frac{1}{1000}$ grain yields a good deposit, which soon, especially if the mixture be stirred, assumes the crystalline form.

3. $\frac{1}{5000}$ grain yields no indication, even after the mixture has stood some time.

The crystalline form of the double atropine salt, as figured above, readily distinguishes it from other substances. The formation of these crystals, however, is readily prevented by the presence of foreign organic matter.

5. *Iodine in Potassium Iodide.*

A solution of iodine in potassium iodide throws down from solutions of salts of atropine, and of the free alkaloid, a reddish-brown, amorphous precipitate, which is insoluble in acetic acid, and only sparingly soluble in potassium hydrate.

1. $\frac{1}{100}$ grain of atropine yields a very copious precipitate, which dissolves to a clear solution in about three drops of a saturated solution of potassium hydrate.

2. $\frac{1}{1000}$ grain: a quite copious precipitate.
3. $\frac{1}{10,000}$ grain yields a very good deposit.
4. $\frac{1}{50,000}$ grain yields at first a yellowish turbidity, and after a little time a distinct, reddish-brown precipitate.
5. $\frac{1}{100,000}$ grain yields a very distinct turbidity.

The reaction of this reagent is common to a large class of substances.

Other Reagents.—Dr. D. Vitali has lately shown (1880) that if atropine or any of its salts in the solid state, placed in a porcelain capsule, be heated with a few drops of *nitric acid*, and then the liquid evaporated at a moderate temperature, the cooled colorless residue on being touched with a drop of a concentrated *alcoholic* solution of *potassium hydrate* will assume a splendid violet or purple color, even if only a minute quantity of the alkaloid be present. After a little time this color disappears; but it may be reproduced upon the further addition of the alcoholic solution of the caustic alkali.

We find that under this test 1–1000th grain of atropine will yield a fine purple coloration, which may be reproduced on adding a second drop of the alkaline alcoholic solution. And the 1–25,000th of a grain yields a perfectly satisfactory purple coloration. A marked purple coloration may be obtained from even the 1–50,000th of a grain of the alkaloid, especially if the alkaline alcoholic solution be added to the nitric acid residue while still warm.

The reaction of this test is common, we find, to atropine, daturine, hyoscyamine, and duboisine. Of some sixty other alkaloids examined under this test by Dr. D. Vitali, he found none to give the same reactions as atropine and daturine.

According to Dr. A. W. Gerrard (*Pharm. Jour. and Trans.*, March, 1884, 718), if a little atropine in a test-tube be treated with a small volume of a 5 per cent. solution of mercuric chloride in 50 per cent. alcohol, and the mixture gently warmed, a brick-red precipitate will be produced. The precipitate has, according to Dr. Gerrard, the composition $C_{17}H_{23}NO_3,HCl,2HgCl_2$, and may be obtained in the crystalline state. The precipitate, however, does not appear in dilute solutions of the alkaloid. Dr. Gerrard found this reaction to be also common to daturine, hyoscyamine, duboisine, and

homatropine; but of a number of other alkaloids examined none gave a red precipitate.

Tannic acid produces in solutions of salts of atropine a dirty-white, amorphous precipitate, which is readily soluble in the caustic alkalies and in free acids. One grain of a 1–100th solution of the alkaloid yields a copious deposit; and a similar quantity of a 1–1000th solution a quite distinct reaction. *Platinic chloride* and *palladic chloride* throw down from concentrated solutions of salts of the alkaloid dirty-brown, amorphous precipitates. Strong solutions of salts of atropine, when treated with a stream of *chlorine gas*, become slightly turbid, and yield on the subsequent addition of ammonia a white precipitate.

Potassium iodide, potassium sulphocyanide, potassium chromates, mercuric chloride, mercurous nitrate, potassium ferro- and ferricyanide, and gallic acid fail to precipitate even concentrated solutions of salts of atropine.

Physiological Test.—The property possessed by atropine of dilating the pupil of the eye has been proposed as a means of detecting its presence. Dr. Headland states (*Action of Medicine*, 294) that the 1–3000th of a grain of the alkaloid dropped, in the form of solution, into the eye of an adult will answer this purpose. It must be borne in mind, however, that this property is also possessed by daturine, hyoscyamine, duboisine, and certain other alkaloids.

Separation from Organic Mixtures.

Suspected Solutions and Contents of the Stomach.—These should first be carefully examined for the presence of any solid portions of the plant or the seeds, which, if found, may be identified by their physical and botanical characters. On account of the indigestible nature of the seeds and berries, they may remain in the alimentary canal for some days without undergoing any change. Dr. Christison cites several instances (*op. cit.*, 644) in which the seeds and fragments of the fruit were discharged from the bowels and by vomiting, even several days after they had been taken.

Atropine is separated with considerable difficulty from complex organic mixtures, especially when it exists in the form of portions of the plant. The suspected mixture, after comminution of any solids present, and dilution if necessary, is treated with about an equal volume of strong alcohol, slightly acidulated with sulphuric acid,

and exposed for about half an hour to a gentle heat; when cool, the liquid portion is strained through muslin, the residue washed with alcohol, and the strained liquid and washings concentrated to a small bulk, at a moderate temperature, on a water-bath. If during the evaporation much insoluble matter separates, it is removed by a strainer. The cooled concentrated liquid is passed through a moistened filter, then washed by agitating it with about twice its volume of pure *ether*, which, after repose, is carefully decanted and reserved for future examination, if necessary; the aqueous solution may again be washed with a fresh portion of ether, and this removed as before. The aqueous liquid is now rendered slightly alkaline by potassium hydrate or carbonate, and thoroughly agitated with about twice its volume of pure *chloroform*, which will dissolve the liberated alkaloid, if present; after the liquids have completely separated, the chloroform is carefully removed to a glass capsule and allowed to evaporate spontaneously.

The residue thus obtained is stirred with a little water containing a trace of sulphuric acid, and the solution, after filtration if necessary, examined by some of the liquid tests for atropine. As the bromine test is one of the most characteristic yet known for the identification of the alkaloid, it should first be applied to a single drop of the solution. Another drop of the solution may be evaporated to dryness and the residue examined by Vitali's test. If the bromine reagent should fail to produce a crystalline precipitate, it is quite certain that neither of the other liquid tests would produce crystals, without which the results are common to a large class of organic substances. It must not, however, be expected that the bromine reagent will always produce a crystalline deposit containing all the forms obtained from a perfectly pure solution of atropine: most frequently, under the present conditions, the precipitate consists of short, opaque, irregular needles and granules, but these are characteristic of the alkaloid.

In case the bromine reagent produces a precipitate which will not crystallize, the remaining portion of the solution may be rendered alkaline, and the alkaloid again extracted by chloroform. This fluid may now, upon spontaneous evaporation, leave the alkaloid, if present in very notable quantity, in the crystalline state. A portion of the residue may be submitted to the physiological test for the alkaloid.

On applying the method now considered to the examination of the contents of the stomachs of animals to which comparatively small quantities of a fluid extract of belladonna had been added, we in every instance obtained perfectly satisfactory evidence of the presence of atropine.

Atropine may also be recovered from organic mixtures by the use of *ether*, the steps of the process being precisely the same as when chloroform is employed. The alkaloid, however, is much less readily extracted from organic liquids by ether than by chloroform.

From the Blood.—Absorbed atropine may be recovered from the blood by acidulating the latter with sulphuric acid, in the proportion of about one drop of the acid to each fluid-ounce of blood, and agitating it with something more than its own volume of alcohol. The mixture is then gently heated for about fifteen minutes, and the liquid, after cooling, strained through muslin, and the residue washed with alcohol and strongly pressed. The strained liquid is concentrated, at a moderate temperature on a water-bath, again strained, then evaporated to a small volume, the filtered liquid rendered alkaline, and the liberated alkaloid extracted by chloroform. If the chloroform residue is not sufficiently pure for testing, it is extracted, in the usual manner, a second time by that liquid.

Three fluid-ounces of blood, taken from a dog that had been given five drachms of Tilden's fluid extract of belladonna and killed by a blow on the head one hour and a half afterward, when examined by the foregoing method, furnished very satisfactory evidence of the presence of atropine. A similar quantity of the extract being administered to a cat, a portion passed into the lungs of the animal, and caused death in less than three minutes. Five drachms of blood taken from this animal also furnished satisfactory evidence of the presence of the alkaloid.

Section III.—Daturine. (Stramonium.)

History.—Daturine is the name applied to the active principle, or alkaloid, of *Thorn-apple*, *Jamestown weed*, or *Datura stramonium*. The existence of this principle was announced in 1819 by Brandes; but it was first obtained in 1833 by Geiger and Hesse. It is found in all parts of the plant, but most abundantly, it is said, in the

seeds and fruit. Its composition is $C_{17}H_{23}NO_3$, it being identical in composition with atropine.

Preparation.—Daturine may be obtained from the bruised seeds of stramonium, and other parts of the plant, in the same manner as atropine is prepared from belladonna, as heretofore described (*ante*, 631). The proportion of the alkaloid present in the plant is, perhaps, about the same as that found in belladonna.

Numerous instances of poisoning by *stramonium*, more particularly by the seeds, have occurred, but, with few exceptions, they have been the result of accident. As yet there seems to be no instance in which *daturine* in its pure state has been taken as a poison.

Symptoms.—The symptoms produced by stramonium are very similar to, if not identical in kind with, those occasioned by belladonna. Thus, they are dryness of the throat, difficulty of deglutition, dilatation and insensibility of the pupil, headache, nausea, vomiting, great thirst, obscurity of vision, or total blindness, ringing in the ears, great anxiety, hot skin, flushed countenance, vertigo, and wild delirium, with spectral illusions, and tremors of the extremities, followed by stupor and coma. Occasionally convulsions and paralysis have occurred, as also a scarlet eruption over the skin.

In a case reported by Dr. J. G. Johnson, of Brooklyn, N.Y., a boy, seven years of age, ate a quantity of the green seeds of stramonium, picking them from the burs. The first symptoms observed were impaired speech, flushed face, twitchings of the fingers, and a staggering gait. About two hours and a half after taking the poison the child was in a state of violent agitation, and had spasmodic twitchings of the hands, as if affected with chorea; the pupils were enormously dilated and insensible to light, and there was total blindness; the face, especially around the mouth, was much swollen; the action of the heart was feeble, and the pulse could not be counted; the lower extremities were cold, and perfectly powerless. The action of an emetic now brought away a quantity of the seeds. Two hours later, the child was violently maniacal, constantly catching at imaginary objects in the air, was also deaf, and unable to articulate. These symptoms gradually abated, but it was several days before the patient entirely recovered, the insensibility of the pupils continuing until the fourth day. (*American Medical Times*, 1860, i. 22.)

Dr. H. Y. Evans, of Philadelphia, has reported an instance in which seven children, aged from six to nine years, had each swallowed,

it is said, only ten of the seeds. Four hours afterward, the pupils in all seven cases were dilated to their utmost. In three of the children, who had swallowed the seeds without chewing them, dilatation of the pupils and slight perversion of vision were the only effects observed. But in the four remaining cases, in which the seeds had been chewed, in addition to the dilated state of the pupils and perverted vision there was confusion of intellect, deafness, intoxication, full pulse, slow respiration, and entire loss of power to direct the motions of the limbs; these symptoms were succeeded in a few hours by stupor, and in one case by violent delirium, resembling delirium tremens. Emetics having failed to act, except in the three slight cases, the stomach was emptied by means of the stomach-pump, and on the third day every vestige of the poisoning had disappeared, the pupils being the last to yield. (*Amer. Jour. Med. Sci.*, July, 1866, 278.)

A somewhat similar instance to that just cited has been reported by Dr. A. P. Turner. (*Ibid.*, April, 1864, 552.) Of seven children who had eaten a quantity of the seeds, in five vomiting was early produced, and they were but slightly affected. In the other two, the most violent symptoms with wild delirium manifested themselves; but, under the use of emetics, and laudanum, the patients were quite well on the third day. In a case related by Dr. Calkins, a child, four years of age, entirely recovered after having swallowed over a tablespoonful of the seeds, although they remained undisturbed in the body for upwards of seven hours, when they were partly ejected by vomiting, and afterward partly by purging. (*American Medical Monthly*, Sept. 1856, 220.)

Dr. C. C. Lee has related an instance (*Amer. Jour. Med. Sci.*, Jan. 1862, 54) in which three adults were poisoned by an alcoholic decoction of the seeds of stramonium. Soon after taking the poison two of the patients were speechless, unable to walk, and in a comatose condition; their faces flushed to an almost violet hue, the conjunctivæ injected, the pupils enormously dilated and insensible, the face and upper extremities burning hot, the tongue and throat dry, the respiration slow and labored, and the pulse rapid, very tense and full. In the other case, in which a smaller quantity of the decoction had been taken, the skin was of a scarlet hue and hot, the pupils dilated, the tongue parched, the respiration hurried, the pulse very rapid, and fluttering, and there was intense thirst, with violent delirium, the patient constantly pursuing with her hands imaginary objects in the

air, or picking at the bedclothes. About an hour and a half after the poison had been taken, active treatment, including the use of the stomach-pump, was resorted to, under which all the patients rapidly recovered.

In a fatal case, quoted by Dr. Christison (*On Poisons*, 646), in which a child, aged two years, had swallowed, without chewing, about one hundred of the seeds, the following symptoms were observed. The child soon became fretful and like a person intoxicated; in the course of an hour efforts to vomit ensued, together with flushed face, dilated pupils, incoherent talking, and afterward wild spectral illusions and furious delirium. In two hours and a half there was loss of voice and the power of swallowing; then croupy breathing and complete coma set in, with violent spasmodic agitation of the limbs, occasional tetanic convulsions, warm perspiration, and an imperceptible pulse. Subsequently the pulse became extremely rapid, the abdomen tympanitic, and the bladder paralyzed, but there were frequent involuntary stools; and death took place twenty-four hours after the poison had been taken. At an early period in the case, twenty of the seeds were discharged by an emetic; and afterward eighty by purging: none were found in the alimentary canal after death. In another case, a decoction of about one hundred and twenty-five of the seeds proved fatal to an elderly woman in seven hours. In a case related by Dr. Allan, an unknown quantity of the seeds caused the death of a healthy man in about seven hours and a half. (*Lancet*, London, Sept. 1847, 298.) Three non-fatal cases of stramonium poisoning in children have recently been reported by Dr. Herbert Terry. (*Boston Med. and Surg. Jour.*, Feb. 1882, 123.)

The *external application* of stramonium to a blistered surface has in several instances given rise to alarming symptoms. In one instance, the *extract* employed as a suppository induced many of the symptoms of delirium tremens. Even bruising the leaves in a mortar has caused dilated pupil and irritation of the skin. (*Beck's Med. Jur.*, ii. 877.)

Treatment.—This is the same as in poisoning by belladonna (*ante*, 638). In a case of stramonium poisoning quoted by Dr. A. Stillé (*Mat. Med.*, i. 754), one grain of morphine hydrochloride was administered every hour, and eight grains were taken before any result was perceived. After the eighth dose slight signs of awakening consciousness were visible, but the pupil still remained widely

dilated. Subsequently, as the symptoms abated, the intervals between the doses were lengthened, but in the course of eighteen hours *fifteen grains* of the morphine salt were taken.

Post-mortem Appearances.—In the case of the child, heretofore cited, in which death occurred in twenty-four hours, the brain was found natural, the stomach and intestines healthy, the bladder distended, the larynx and œsophagus slightly reddened, the rima glottidis thickened and very turgid, and the blood throughout the body semi-fluid. In Dr. Allan's case, nineteen hours after death, there was found great turgescence of the membranes of the brain; the brain itself was firm and highly injected, the choroid plexus turgid, and the ventricles contained a little bloody serum. The lungs were very vascular, and the heart flaccid. The stomach contained about four ounces of ingesta, in which were found eighty-nine entire seeds of stramonium, together with many fragments. The mucous membrane of the stomach throughout was slightly congested, and presented two patches of extravasation, the one being in the greater curvature of the organ, and the other near the pyloric orifice. Many of the poisonous seeds, as well as fragments, were also found throughout the entire length of the small intestines. The liver, spleen, pancreas, bladder, and kidneys were normal.

Chemical Properties.

Daturine is not only identical with *atropine* in regard to its elementary composition, but is also possessed, as first announced by Planta (*Chem. Gaz.*, 1850, 350), of the same physical and chemical properties. The chemical reactions of atropine and the methods of separating it from organic mixtures, as already described, are, therefore, equally applicable for the detection of daturine.

The identity of these two alkaloids, in regard both to their properties and physiological effects, is now generally conceded. Hence it is obvious that, unless some compound is discovered to exist in the one plant that is not present in the other, there can be no *chemical* means of distinguishing between poisoning by belladonna and by stramonium. This can be done only when portions of the plant are found and identified by their physical and botanical characters, or by a knowledge of the attending circumstances.

Further, it is now generally admitted that *all* of the *mydriatic* alkaloids have the same elementary composition, namely, $C_{17}H_{23}NO_3$;

but it is still held by some that at least certain of them differ somewhat in their properties. According to the recent researches of Prof. Landenburg, there are three distinct but closely allied principles of this kind, namely, *Atropine*, *Hyoscyamine*, and *Hyoscine*. Under the name *Hyoscyamine* he includes as fully identical the alkaloids formerly known as *hyoscyamine*, *daturine*, and *duboisine*, the first derived from *Hyoscyamus niger* (henbane), and the last-named from *Duboisia myoporoides*. *Hyoscine* is found, according to Prof. Landenburg, only in *Hyoscyamus niger*, associated with *hyoscyamine*.

On examining comparatively samples of *atropine*, *daturine*, *hyoscyamine*, and *duboisine*, as prepared by well-known manufacturers, we in no instance found any essential difference in their chemical properties with reagents. Thus, they all gave similar crystalline precipitates with *bromine*, and the same color reaction under *Vitali's test*, and like results with other reagents.

Extraction from Aqueous Mixtures.—When one grain of *daturine* was dissolved, by the aid of a gentle heat, in four hundred grains of pure water, and the solution agitated with four volumes of *chloroform*, this liquid left upon spontaneous evaporation 0.88 of a grain of the pure alkaloid. When a similar aqueous solution was agitated with four volumes of absolute *ether*, this fluid extracted 0.80 of a grain of the alkaloid. On extracting alkaline complex organic mixtures containing small quantities of a fluid *extract* of stramonium, by chloroform, we obtained about the same results as already described from similar mixtures containing the extract of belladonna.

One ounce of *blood*, taken from a cat killed by half an ounce of *Tilden's fluid extract* of stramonium, when subjected to the same treatment as described for the recovery of atropine under similar circumstances, furnished a final chloroform residue which gave unequivocal evidence of the presence of the alkaloid.

CHAPTER V.

VERATRINE, JERVINE, SOLANINE.

Section I.—Veratrine. Jervine. (White and American Hellebores.)

History.—*Veratrine* is a highly poisonous alkaloid, found in *Veratrum sabadilla*, and in *Cevadilla*, the seeds of *Asagræa officinalis;* also in *Veratrum album*, or White hellebore, and *Veratrum viride*, or American hellebore. This alkaloid was first obtained from sabadilla by Meissner, of Germany, in 1819; and about the same time, from the same source, by Pelletier and Caventou, of France. In 1820, the latter chemists obtained from the rhizoma of *Veratrum album* an alkaloid which they regarded as identical with veratrine; and in 1838, Mr. Worthington announced its existence in the root of *Veratrum viride.*

In 1862, Mr. G. J. Scattergood announced that, in addition to *veratrine*, *Veratrum viride* contained another principle similar in nature to that alkaloid, but insoluble in ether, and a third substance, a resin to which the sedative action of the drug was chiefly due. (*Amer. Jour. Pharm.*, 1863, 74.) On the other hand, Mr. C. Bullock claimed (*ibid.*, 1865, 321) that the alkaloid in question was not identical with *veratrine*, and that the resin of Scattergood owed its activity to the presence of another alkaloid, which, unlike the first, was insoluble in ether. Prof. Geo. B. Wood named these substances respectively *veratroidia* and *viridia*. In 1872, Dr. Peugnet announced (*Med. Record*, May, 1872, 121) that Bullock's *viridia* was identical with *jervine*, first obtained, in 1837, by E. Simon from *Veratrum album.*

Much discrepancy has also existed in regard to the active principle or principles of *Veratrum album.* Thus, in 1820, as already mentioned, Pelletier and Caventou obtained from this plant an alkaloid which they regarded as identical with *veratrine* from sabadilla

seeds; and in 1837, Simon announced the presence of a second principle, which he named *jervine*. In 1872, Dr. Peugnet claimed that the alkaloid other than jervine in white hellebore was not veratrine, but identical with Bullock's *veratroidia* from American hellebore; while still later, Mr. C. L. Mitchell (*Proc. Amer. Pharm. Assoc.*, 1874, 436) claimed that it differed from both veratrine and veratroidia, and proposed for it the name *veratralbia*. In 1876 we obtained from both *Veratrum viride* and *Veratrum album* an alkaloid which fully responded in its reactions to all the tests for *veratrine*. (*Amer. Jour. Pharm.*, 1876, 1.)

More recently, the alkaloids of the Veratrums have been very fully examined by Messrs. Wright and Luff. (*Jour. Chem. Soc.*, 1879, 405.) According to these observers, *Veratrum album* contains *jervine*, *pseudojervine*, *rubijervine*, and *veratralbine*, with a minute quantity of *veratrine;* whilst *Veratrum viride* contains these same principles with the addition of *cevadine* (Merck's veratrine). The proportions of these several alkaloids found in the two Veratrums per kilo. of the roots were about as follows:

	V. album.	V. viride.
Jervine, $C_{26}H_{37}NO_3$	1.3 gram.	0.2 gram.
Pseudojervine, $C_{29}H_{43}NO_7$ . .	0.4 "	0.15 "
Rubijervine, $C_{26}H_{43}NO_2$ . .	0.25 "	0.02 "
Veratralbine, $C_{28}H_{43}NO_5$ . .	2.2 "	only traces.
Veratrine, $C_{37}H_{53}NO_{11}$ . . .	0.05 "	less than 0.004.
Cevadine, $C_{32}H_{49}NO_9$ . . .	apparently absent.	0.43 gram.
	4.20	0.80

According to Wright and Luff, *sabadilla seeds* contain three alkaloids, *veratrine*, *cevadine*, and *cevadilline*, the last being present in only small quantity and having the composition $C_{34}H_{53}NO_8$.

Preparation. *a. Veratrine.*—For commercial purposes, veratrine is usually obtained from the seeds of sabadilla, or cevadilla, as it is frequently called. The bruised seeds, deprived of their capsules, are exhausted by repeated portions of hot alcohol, the mixed alcoholic solutions concentrated to a small volume, then treated with slight excess of ammonia, and the impure precipitated alkaloid washed with cold water; it is then boiled for some little time with water acidulated with hydrochloric acid and containing animal charcoal, the cooled solution filtered, the concentrated filtrate rendered slightly alkaline by ammonia, the precipitate thus produced washed with

water, and then dried on a water-bath. The product thus obtained may be further purified by dissolving it in water acidulated with hydrochloric acid, and extracting the foreign organic matter by ether: after decanting this liquid, the aqueous solution is treated with slight excess of ammonia, and the liberated alkaloid extracted by fresh ether, which is allowed to evaporate spontaneously, when the veratrine will be left in its very nearly pure, but amorphous or, at most, granular, state.

Instead of the use of alcohol for the extraction of the alkaloid from the bruised seeds, Dr. Thomson, of Edinburgh, has proposed to treat them with boiling water acidulated with hydrochloric acid, and allow the whole to stand twenty-four hours. The liquid is then expressed, filtered, concentrated to a small volume, and treated with slight excess of ammonia. The precipitate thus produced is collected on a filter, washed, and dried, then pulverized and extracted with hot alcohol. The alcoholic solution is distilled until the spirit is entirely expelled, the residue heated with acidulated water and animal charcoal, and the filtered solution rendered slightly alkaline by ammonia, when the veratrine will be precipitated in the form of a nearly pure-white powder. (*Chemical News*, June, 1861, 334.) By this method Dr. Thomson obtained at the rate of twenty grains of the alkaloid from one avoirdupois pound of the seeds. From one pound avoirdupois of the dried root of *Veratrum viride* Mr. G. J. Scattergood, of Philadelphia, obtained about thirty grains of nearly pure mixed alkaloids.

b. Jervine.—Jervine may be obtained from *Veratrum viride* by preparing a strong alcoholic solution of the roots and treating this with several volumes of water. When the resinous matter has deposited, the clear liquid is evaporated to a small volume, filtered, and the filtrate treated with slight excess of sodium carbonate. The precipitate of the mixed alkaloids thus produced is extracted with *ether*, which, after decantation, is allowed to evaporate spontaneously, small portions at a time, in a deep glass capsule. The jervine will now be found chiefly in the bottom of the capsule, in the form of bold groups of crystals, Plate XIV., fig. 3; while the amorphous alkaloids will remain chiefly in the upper portion of the deposit, as a more or less yellowish, transparent, vitreous mass.

The residue thus obtained is treated with a little water strongly acidulated with hydrochloric acid (1 : 10), which will readily dissolve

the amorphous alkaloids, whilst the jervine will remain as hydrochloride. The mixture is transferred to a moistened filter, and the jervine residue washed with a little acidulated water. The washed residue is now digested with sodium carbonate solution, when the alkaloid will be set free. This is collected on a filter, and then dissolved in a little water strongly acidulated with acetic acid. The acetic acid solution is rendered alkaline by sodium carbonate, and the liberated alkaloid extracted with *chloroform*. If the chloroform residue is amorphous, it may be converted into the crystalline state by moistening it with a little diluted alcohol.

Poisoning by *veratrine*, in its pure state, has been of extremely rare occurrence, and as yet in no instance, so far as we know, has it been taken in fatal quantity by the human subject. But poisoning by portions of some of the different plants which owe their activity, at least in part, to the presence of this alkaloid, has not unfrequently happened, as the result of accident. There seems to be no instance on record of criminal poisoning by this substance. The ordinary medicinal dose of the commercial alkaloid is about one-tenth of a grain.

Symptoms.— *White hellebore* root has long been known as a poison. When taken in poisonous quantity, the more usual effects are a sense of burning heat in the stomach, with a feeling of constriction and heat in the mouth and throat, great anxiety, nausea, violent vomiting, purging, tenesmus, pain in the bowels, trembling of the limbs, great prostration, cold sweats, small and feeble pulse, vertigo, dilated pupils, loss of sight, impaired speech, coldness of the extremities, convulsions, and insensibility. These symptoms are never, perhaps, all present in the same case. Thus, instances are recorded in which purging was absent, and others in which there was no vomiting. This substance has not unfrequently occasioned death. In non-fatal cases, the symptoms are sometimes very slow in disappearing.

In an instance cited by Dr. Christison, in which three persons had taken a quantity of the root, and finally recovered, the following symptoms were observed. In the course of an hour all the patients experienced a sense of burning in the throat, gullet, and stomach, followed by nausea, dysuria, and vomiting; weakness and stiffness of the limbs; giddiness, blindness, and dilated pupil; great faintness, convulsive breathing, and small pulse. One of them, an elderly woman, who had taken the largest quantity, had an imperceptible

pulse, stertorous breathing, and total insensibility; on the following day an eruption appeared over the body. (*On Poisons*, 673.) Two children, aged three and a half and one and a half years respectively, drank of a decoction of white hellebore. The principal symptoms were violent vomiting, insensibility, a pale and sunken countenance, small sharp pulse, heat of head and coolness elsewhere, slight spasmodic movements of the face and limbs, neck somewhat swollen, deglutition impossible, pupils dilated, and the eyes staring. Both children recovered. (Stillé, *Mat. Med.*, ii. 314.)

Dr. E. Peugnet has very fully reported (*Med. Record*, May, 1872, 124) the case of a young married lady, who by mistake swallowed a quantity of a tincture of veratrum album, equivalent to half a drachm of the powdered root. No symptoms appeared for three hours; but four hours after taking the dose she was found pulseless, the heart pulsating feebly and irregularly; the respiration was slow. The eyes were fixed and staring, the pupils dilated, and there was almost total loss of sight. The body was covered with a cold and clammy perspiration, and there was complete anæsthesia of the skin; the lips were bright carmine; the mind was clear, calm, and collected; there was incessant vomiting and retching, the fluid ejected being a viscid, glairy mucus, of a greenish hue. Shortly afterward there was violent purging accompanied with severe tenesmus. Violent symptoms continued for several weeks, but finally the patient fully recovered.

In a fatal case, in which a man had taken only a small quantity of the powdered root, the patient was soon seized with violent and incessant vomiting, and died within twelve hours. In an instance quoted by Dr. Taylor (*On Poisons*, 575), twenty grains of the powder caused convulsions, and death in three hours. The external application of hellebore to the epigastrium has caused violent vomiting. So, also, its employment in the form of enema has given rise to violent symptoms.

American hellebore, familiarly known as Indian poke, has not unfrequently produced alarming and even, in a few instances, fatal results. All parts of the plant have a nauseous, bitter taste, followed by a persistent acrid sensation in the mouth and throat. The symptoms occasioned by an overdose of this substance are very similar to those produced by white hellebore. In a case reported by Dr. J. C. Harris, of West Cambridge, a feeble child, one and a

half years old, was ignorantly given four drops of the tincture of veratrum viride mixed with water every half-hour, until four or five doses had been taken, when by mistake a dose containing about sixteen drops was administered. Repeated efforts to vomit ensued after the administration of the second dose, but without success, except once, when a small quantity of matter was ejected from the mouth. Seven hours after taking the first dose the child was apparently unconscious, very pale, and breathing stertorously; the pulse was very slow, the extremities cold, and a profuse perspiration covered the whole body. Treatment was now resorted to, but without any attempt to remove the contents of the stomach. The symptoms increased in violence, and death ensued in about thirteen hours after the first dose had been given. (*Amer. Jour. Med. Sci.*, July, 1865, 284.)

Dr. T. M. Johnson, of Buffalo, has related an instance in which he made a post-mortem examination of the body of a woman whose death was stated to have been produced by two doses of Tilden's fluid extract of veratrum viride. It seems that the woman, who was fifty years old and quite infirm, had taken at first a dose of about thirty drops of the extract, and in about two hours was seized with considerable pain in the stomach, nausea, and vomiting. From four to six hours after taking the first dose she took another and larger one, probably about forty-five drops. This was followed within two hours by severe pain in the epigastrium, retching, vomiting, weak and rapid pulse, and marked prostration; and within twelve hours she had two or three bloody stools with considerable tenesmus. Diarrhœa continued a few hours after the subsidence of the dysenteric discharges; but the retching and vomiting continued at intervals for about four weeks, when she died. No abnormal appearance was detected in the body, except that the stomach was much less in size than usual. (*Buffalo Med. and Surg. Jour.*, Nov. 1866, 133.)

In an instance related by Dr. J. B. Buckingham (*Amer. Jour. Med. Sci.*, Oct. 1865, 563), two gentlemen, through mistake, swallowed each about a teaspoonful of a fluid extract of the American hellebore. In about half an hour one of the patients was found almost speechless, retching and vomiting incessantly, bathed in profuse cold perspiration, and with a scarcely perceptible pulse. On the administration of a teaspoonful of laudanum the vomiting ceased, and the patient rapidly recovered. In the other case, in

which the laudanum was not administered, the vomiting continued for some hours, with total loss of speech and of locomotion for some time.

Dr. Geisen reports (*Med. and Surg. Reporter*, Dec. 1870, 453) the case of a lady, aged sixty years, suffering from hepatic distress, with occasional vomiting, for which were prescribed ten drops of Norwood's tincture of veratrum viride every three hours. Although vomiting terribly after each dose, the patient continued taking the medicine until six doses were taken. Shortly after taking the sixth dose she sank and died from the effects of the poison. In a case related by Dr. M. Marsh (*ibid.*, May, 1873, 379), a man affected with pleuro-pneumonia swallowed, through ignorance, thirty-three minims of the tincture. He was found soon after pulseless, insensible, and in a cold sweat, with frequent spasmodic jerkings of the arms, and died in convulsions six hours thereafter.

A case of this kind, fatal in a few hours, is reported by Dr. R. M. Kirk (*ibid.*, July, 1879, 63), in which a man, aged thirty years, drank a quantity of the tincture of veratrum viride, mistaking it for whiskey. Dr. G. Sykes reports a non-fatal case (*Louisville Med. News*, 1880, 115) in which eighty minims of the tincture with one-hundred and sixty minims of tincture of gelsemium had been taken. A case is related in which an ointment of veratrum viride applied to an ulcer on the leg produced vomiting.

In a recent case reported by Dr. L. N. Horwitz (*Med. Times*, Aug. 1884, 863), a teaspoonful of the officinal tincture of veratrum viride, given in mistake to a patient convalescing from typhoid fever, caused his death some hours afterward. In this case the fatal termination was apparently largely due to the prostrated condition of the patient at the time the poison was taken.

Veratrine, as found in the shops, is subject to great variation in strength. In a case communicated to Dr. Taylor, one-sixteenth of a grain of the alkaloid nearly proved fatal to a lady. Not long after the dose had been taken the patient was found insensible, the surface cold, the pulse failing, and there was every symptom of approaching dissolution. (*On Poisons*, 576.) In a case mentioned by Dr. S. R. Percy, a physician took, by mistake, thirty grains of the crude alkaloid prepared from veratrum viride. It caused copious vomiting, followed by prostration and loss of pulse at the wrist; but under the free use of stimulating remedies the patient entirely

recovered on the third day. (*Prize Essay*, 1864, 76.) Dr. C. P. Blake relates a case (*St. George's Hosp. Rep.*, 1870, 69) in which a woman, by mistake, swallowed three grains of veratrine, made into a liniment with glycerine, chloric ether, and laudanum. Under treatment she speedily recovered.

Experiments.—Two grains of nearly colorless commercial veratrine being administered in solution to a healthy cat, the animal was immediately rendered prostrate, frothed at the mouth, and died in less than one minute after taking the dose. A similar quantity given to a second cat produced similar symptoms, and death in one minute and three-quarters. Three grains of the same preparation given to a young dog caused immediate vomiting, which was frequently repeated, with purging, involuntary urination, and great prostration, followed by death in two hours after the administration of the dose. Of another sample of the commercial alkaloid, two grains each were given to two small dogs without producing any appreciable symptom other than slight prostration, from which the animals soon recovered.

Treatment.—This consists in the speedy removal of the poison from the stomach, and the subsequent exhibition of stimulants. Opium has in several instances been found highly beneficial. No chemical antidote is as yet known. Vegetable infusions containing tannic acid have been strongly advised. Although this vegetable acid forms with veratrine a compound that is only very sparingly soluble in water, yet it is very readily soluble in the presence of a free acid. In some instances purgatives may be found highly useful.

Post-mortem Appearances.—In the few cases that have been examined, in death from this substance, the alimentary canal was more or less inflamed; but nothing has been observed characteristic of the action of the poison. In animals killed by commercial veratrine, Esche found the throat and œsophagus pale; the stomach and bowels more or less contracted, and the latter somewhat reddened; and the lungs, liver, and heart gorged with blood. The brain presented nothing abnormal. (Stillé, *Mat. Med.*, ii. 312.)

Chemical Properties.

a. Veratrine.

In the Solid State.—*Veratrine*, when perfectly pure, is a colorless, odorless solid, which may be obtained, not readily, however,

in the form of transparent crystalline prisms. It has an exceedingly acrid but not bitter taste, followed by a persistent sense of dryness and acridity in the fauces. When snuffed into the nostrils, even in only very minute quantity, it occasions most violent and prolonged sneezing. As found in the shops, veratrine is usually in the form of a dull white or yellowish-white, amorphous powder, having an intensely acrid, more or less bitter taste. The impure alkaloid is much more apt, on handling, to become diffused in the air and excite sneezing than the pure base. According to Dr. A. Wright, the sternutatory constituent of Veratrum viride is cevadine.

When applied, in the form of an alcoholic solution, to the sound skin, veratrine occasions a sense of heat, redness, and pricking in the part. Heated on porcelain or in a glass tube, the pure alkaloid fuses to a brownish transparent liquid, swells up, and is slowly dissipated, under decomposition, without any residue; heated in a direct flame, it takes fire and burns with dense smoke. Its fusing point, according to Couerbe, is 115° C. (239° F.).

If a small quantity of *pure veratrine* be touched with a drop or two of cold concentrated *sulphuric acid*, it assumes a yellow color, then a reddish tint, and slowly dissolves to a pinkish solution, which after several minutes acquires a deep crimson-red color. These changes are brought about almost immediately by the application of heat. This is one of the most characteristic reactions of veratrine yet known (see *post*).

Concentrated *hydrochloric acid* dissolves the pure alkaloid without change of color; but if the solution be heated to the boiling temperature, as first observed by Merck and afterward more minutely by Trapp, of St. Petersburg, it quickly acquires a red color, which ultimately becomes very intense and resembles that of a solution of potassium permanganate. Under this reaction, if only a drop of the acid be employed, almost the least visible quantity of the alkaloid will manifest itself. With minute quantities, the coloration is best observed by performing the experiment in a white porcelain dish.

The pure alkaloid is also soluble without change of color in concentrated *nitric acid*. But, under the action of this acid, the alkaloid as found in the shops usually acquires a yellow or reddish color and dissolves to a more or less yellowish solution.

Veratrine has strong basic properties, completely neutralizing even the most powerful acids to form *salts*, but few of which have

as yet been obtained in the crystalline state. The sulphate, hydrochloride, tartrate, and oxalate are said to have been thus obtained. The double salts of the alkaloid with mercuric and auric chlorides may be obtained crystallized; as also the simple hydrobromide. The uncrystallizable salts form colorless gum-like or vitreous masses. All the salts of veratrine have the intensely acrid taste of the pure alkaloid.

Solubility.—When large excess of pure veratrine was digested for several hours, with frequent agitation, in *pure water* at the ordinary temperature, one part of the alkaloid dissolved in about 7860 parts of the liquid. *Absolute ether,* under the foregoing conditions, dissolved the pure alkaloid in the proportion of one part in 108 parts of the fluid. Veratrine is very freely soluble in *chloroform,* and also in *alcohol.* The solubility of commercial veratrine in these different liquids is subject to great variation. The alkaloid is readily soluble in water containing a free acid; but it is only very sparingly soluble in the caustic alkalies.

Extraction.—One grain of pure veratrine was dissolved by the aid of just sufficient hydrochloric acid in one hundred grains of water, the solution rendered slightly alkaline by potassium hydrate, and the gelatinous mixture violently agitated with an equal volume of pure *ether;* this liquid was then separated and allowed to evaporate spontaneously, when it left a transparent vitreous residue of 0.89 of a grain of the pure alkaloid. *Chloroform* under similar conditions extracted 0.98 of a grain of the alkaloid, which it left on spontaneous evaporation, in the form of a transparent glacial mass, easily pulverizable to a highly electrical powder.

The *salts* of veratrine are, for the most part, freely soluble in water, but insoluble, or very nearly so, in ether; they are somewhat soluble in chloroform. When one grain of the alkaloid in the form of *hydrochloride* is dissolved in one hundred grains of water, and the solution agitated with an equal volume of pure *ether,* this fluid extracts 0.03 of a grain of the salt. Under similar conditions, *chloroform* extracts 0.31 of a grain of the salt, which it leaves, on spontaneous evaporation, in the form of a colorless, vitreous mass.

Of Solutions of Veratrine.—In the following examination of the behavior of solutions of veratrine, as well as in the preceding investigations, a perfectly colorless and partly crystalline sample of the alkaloid was employed. The solutions were prepared by dis-

solving the alkaloid in pure water, by the aid of the least possible quantity of hydrochloric acid. The fractions employed indicate the fractional part of a grain of the anhydrous alkaloid present in one grain of the solution; the results, unless otherwise indicated, refer to the behavior of one grain of the solution.

1. *The Caustic Alkalies.*

The caustic alkalies, as also their monocarbonates, throw down from solutions of salts of veratrine, when not too dilute, a white, amorphous precipitate of the free alkaloid, which is only sparingly soluble in excess of the precipitant, but readily soluble in diluted acetic acid. After a time, especially if the mixture be stirred, the precipitate becomes more or less granular.

1. $\frac{1}{100}$ grain of veratrine, in one grain of water, yields a very copious precipitate, which after a little time becomes converted into small granules.
2. $\frac{1}{1000}$ grain yields a very good precipitate, which is readily soluble to a clear solution in excess of the precipitant.
3. $\frac{1}{5000}$ grain: if only a mere trace of the reagent be added, the mixture becomes distinctly turbid; if a larger quantity of the precipitant be employed, the alkaloidal solution remains clear.

The true nature of the precipitate produced by these reagents may be established by the following test.

2. *Sulphuric Acid.*

The colorless salts of veratrine, as well as the free alkaloid, when treated in the *dry* state with concentrated sulphuric acid, *slowly* dissolve to a reddish-yellow or pinkish solution, which *after some minutes* acquires a deep crimson-red color. If the mixture be gently heated, this color manifests itself within a few moments, and remains unchanged for some hours. The color is slowly destroyed by the prolonged action of heat, and, also, by stirring in the mixture a small crystal of potassium dichromate.

The following quantities of the alkaloid were obtained by evaporating one grain of a corresponding solution of the hydrochloride to dryness on a water-bath.

1. $\frac{1}{100}$ grain of veratrine, when gently warmed with a drop of the acid, quickly dissolves to a magnificent crimson solution.
2. $\frac{1}{1000}$ grain yields much the same results as 1.

3. $\frac{1}{10,000}$ grain: if the veratrine deposit be first gently warmed, and then a small drop of the acid be allowed to flow over it, the heat being continued, it almost immediately assumes a deep red color, and quickly dissolves to a solution having a quite distinct red hue.
4. $\frac{1}{50,000}$ grain: when treated as under 3, the deposit assumes a faint reddish tint, and dissolves to a colorless solution.

Even a much less quantity of the alkaloid than the last-mentioned, if collected at one point and touched with a minute drop of the warmed acid, will yield a very distinct coloration.

Fallacies.—It has been objected to this test that several other organic substances also strike a red color with sulphuric acid. But, unless the mixture be heated immediately after the application of the acid, these objections have no force, since all these substances, unlike veratrine, are *immediately* colored by the *cold* acid. Moreover, the colors thus produced differ in tint from that occasioned, even after some minutes, by veratrine. And, furthermore, under the continued action of the acid and heat, they differ greatly from the alkaloid under consideration. The exact behavior of the more prominent of these fallacious substances may be briefly mentioned.

Narceine, when touched with the cold acid, immediately assumes a brown color, which quickly changes to brownish-yellow, then slowly to greenish-yellow; if the mixture be gently heated, the narceine quickly dissolves to a bright, brownish-red solution, which, upon continuation of the heat, darkens in color and finally becomes dark purple-red. *Solanine*, under the action of the cold acid, immediately assumes an orange-brown color, and very slowly dissolves to an orange solution, which, after some hours, acquires a purplish-brown color and yields a brownish precipitate; if the orange-colored solution be heated, it soon darkens, becoming almost black. *Piperine* acquires with the acid an immediate orange-red color, which soon becomes brown; if the mixture be heated, it immediately assumes a very dark brown color. *Salicine* imparts to the acid an immediate crimson-pink hue, which, on the application of a gentle heat, is increased in intensity, then darkens, and finally becomes almost black. *Papaverine* dissolves in the acid to an immediate purple solution, the color of which soon fades; on heating the mixture the color is quickly discharged.

It must be remembered that the intensity of the color produced

by veratrine and sulphuric acid may be more or less modified by the presence of foreign matter; and that this is, perhaps, never wholly absent when the alkaloid is extracted in the ordinary manner from complex organic mixtures.

3. *Auric Chloride.*

This reagent produces in solutions of salts of veratrine a canary-yellow, amorphous precipitate, which is very sparingly soluble, without darkening, in potassium hydrate; it is also only sparingly soluble in acetic and hydrochloric acids. Upon boiling the mixture containing the precipitate, the latter dissolves, but is redeposited unchanged as the liquid cools. The precipitate is readily soluble in alcohol, from which, on slow evaporation, it separates in the form of beautiful groups of yellow, silky crystals.

1. $\frac{1}{100}$ grain of veratrine, in one grain of water, yields a very copious precipitate. If the precipitate from a few grains of the alkaloidal solution be dissolved in a few drops of alcohol, and the alcoholic solution be allowed to evaporate slowly, it soon deposits very delicate crystalline tufts and granules, Plate XIII., fig. 3. The formation of these crystals, however, is readily prevented by the presence of foreign matter.
2. $\frac{1}{1000}$ grain yields a quite good deposit, which is readily soluble to a colorless solution in a few drops of potassium hydrate, but only slowly soluble in large excess of hydrochloric acid.
3. $\frac{1}{10,000}$ grain yields a very distinct precipitate, which is readily soluble by heat, but reproduced as the mixture cools.
4. $\frac{1}{50,000}$ grain: the mixture becomes distinctly turbid.

4. *Bromine in Bromohydric Acid.*

An aqueous solution of bromohydric acid saturated with bromine occasions in solutions of salts of veratrine, and aqueous solutions of the free alkaloid, even when highly diluted, a permanent, yellow, amorphous precipitate, which is only sparingly soluble in diluted acetic and hydrochloric acids. The precipitate is readily decomposed by potassium hydrate. Alcohol dissolves it readily, and on spontaneous evaporation leaves it in the form of groups of bold prismatic crystals.

1. $\frac{1}{100}$ grain of veratrine, in one grain of water, yields a very

copious, bright yellow precipitate, the color of which, on the addition of potassium hydrate, becomes white. The precipitate, when dissolved in alcohol and the liquid allowed to evaporate spontaneously, yields a very good crystalline deposit, Plate XIII., fig. 4.

2. $\frac{1}{1000}$ grain yields a dirty-yellow precipitate, which is readily soluble to a clear solution in potassium hydrate. If the precipitate be dissolved in alcohol and the liquid evaporated spontaneously, the deposit is left in the crystalline form.
3. $\frac{1}{10,000}$ grain yields a greenish-yellow precipitate.
4. $\frac{1}{50,000}$ grain: a quite distinct deposit.
5. $\frac{1}{100,000}$ grain yields a very perceptible turbidity.

5. *Iodine in Potassium Iodide.*

An aqueous solution of potassium iodide containing free iodine throws down from solutions of veratrine, and of its salts, a permanent, amorphous precipitate, which is soluble in alcohol, but only sparingly soluble in acetic and hydrochloric acids. The exact color of the precipitate is determined by the quantity of the alkaloid present.

1. $\frac{1}{100}$ grain of veratrine yields a very copious, reddish-brown precipitate, which, upon the addition of potassium hydrate, assumes a white color.
2. $\frac{1}{1000}$ grain: a copious deposit, which is readily soluble to a clear solution in potassium hydrate.
3. $\frac{1}{10,000}$ grain yields a good, reddish-yellow precipitate.
4. $\frac{1}{50,000}$ grain: a distinct, greenish-yellow deposit.
5. $\frac{1}{100,000}$ grain yields a quite perceptible cloudiness.

6. *Picric Acid.*

An alcoholic solution of picric acid produces in solutions of salts of veratrine, when not too dilute, a yellow, amorphous precipitate, which is soluble in alcohol and in free acids, even acetic acid.

1. $\frac{1}{100}$ grain of veratrine, in one grain of water, yields a very copious deposit.
2. $\frac{1}{1000}$ grain: a quite good, greenish-yellow precipitate.
3. $\frac{1}{5000}$ grain yields a quite distinct turbidity.

7. *Potassium Dichromate.*

This reagent throws down from concentrated solutions of salts of veratrine a yellow, amorphous precipitate, which is insoluble in excess of the precipitant, and only sparingly soluble in diluted acids. The precipitate is readily soluble in strong alcohol.

1. $\frac{1}{100}$ grain of veratrine yields a quite good precipitate, which after a time becomes more or less granular.
2. $\frac{1}{500}$ grain yields a very distinct reaction.
3. $\frac{1}{1000}$ grain: no indication.

Potassium chromate produces a precipitate similar to that occasioned by the dichromate, but the reaction is somewhat less delicate.

Other Reagents.—Potassium sulphocyanide and *Potassium iodide* throw down from concentrated solutions of salts of the alkaloid white, amorphous precipitates, which are readily soluble in acetic acid. *Platinic chloride* and *Potassium ferricyanide* occasion in similar solutions dirty-yellow precipitates. *Potassium ferrocyanide* fails to produce a precipitate. *Corrosive sublimate* throws down from very concentrated solutions a white, amorphous deposit, which is readily soluble in water, and left, on slow evaporation of the liquid, in the crystalline state. *Tannic acid* occasions a white, flocculent precipitate, even in highly diluted solutions of the alkaloid.

b. Jervine.

Properties.—Jervine, when pure, is an odorless solid, which readily crystallizes in the form of colorless, transparent needles and prisms, generally arranged in tufts, bundles, and stellate groups. The crystals contain two molecules of water of crystallization, their composition being, according to Dr. A. Wright, $C_{26}H_{37}NO_3,2H_2O$. The anhydrous alkaloid melts, according to this observer, at about 235° C. (455° F.). The molecular weight of the anhydrous alkaloid is 411.

Jervine is very nearly insoluble in *water,* and is only moderately soluble in *alcohol.* In its crystalline state it is almost wholly insoluble in ether; when mixed with the amorphous alkaloids of the plant, it is quite readily soluble in this liquid. *Chloroform* readily dissolves the alkaloid, and generally leaves it, on spontaneous evapo-

ration, as a transparent, vitreous mass, which immediately becomes crystalline on being touched with a drop of *alcohol.*

Of the *salts* of jervine, the *acetate* and *phosphate* are freely soluble in water; but the *sulphate, nitrate,* and *hydrochloride* are only sparingly soluble in this liquid. According to Mr. Chas. Bullock, the *sulphate* of jervine requires 427 parts, the *nitrate* 266 parts, and the *hydrochloride* 121 parts of water for solution. The solubility of the three last-named salts is greatly diminished by the presence of the corresponding acid in its free state: hence they may thus be precipitated from their aqueous solutions. Alcohol dissolves the salts of jervine in moderate quantity.

Reactions in Solid State.—Concentrated *sulphuric acid* causes pure jervine to assume a yellow color, and quickly dissolves it to a yellow solution, which, becoming reddish-yellow, then dirty-brown, finally assumes a bright *green* color. A very minute portion of the alkaloid will exhibit this coloration. After a time the green color thus produced disappears, and dirty-white or brownish flakes separate. These after a time may become more or less granular or crystalline.

Sulphuric acid produces similar results with the sulphate, hydrochloride, and acetate of the alkaloid; but it dissolves the pure nitrate with an orange-red color, which is more or less permanent for some hours.

Under the action of *sulphuric acid* containing a little *molybdic acid* (Froehde's reagent), pure jervine yields about the same green coloration as with the former acid alone. Nor is the green coloration much modified by stirring in the sulphuric acid solution of the alkaloid a minute crystal of potassium dichromate.

Nitric acid quickly dissolves jervine, under a pinkish coloration, to a colorless solution, from which bold crystals of the nitrate may separate.

Hydrochloric acid fails to produce any coloration or to dissolve the alkaloid, immediately converting it into the insoluble hydrochloride, which becomes, partly at least, crystalline.

Solutions of Jervine.—Jervine is precipitated from its solutions as acetate by various reagents.

1. Dilute *sulphuric acid* (1 : 5) precipitates the alkaloid as sulphate, which is only sparingly soluble in the presence of the free acid. 1–100th grain of the alkaloid, in one grain of liquid, yields

an immediate precipitate, which quickly becomes crystalline, first forming spherical nodules, then groups or brush-like masses of needles, and finally the crystals assume the forms illustrated in Plate XIV., fig. 4. 1–500th grain: immediately crystals begin to separate, and in a little time there is a very good crystalline deposit. 1–1000th grain: microscopic crystals soon appear, and after a time a very satisfactory deposit of long needles separates.

Soluble *sulphates* also precipitate the alkaloid from its acetic acid solutions.

2. *Nitric acid* (sp. gr. 1.2) throws down the alkaloid as nitrate from solutions of the acetate. 1–100th grain of the alkaloid yields a dense precipitate, quickly becoming crystalline, Plate XIV., fig. 5. 1–1000th grain: speedily groups of crystals appear, and after a little time there is a very satisfactory crystalline deposit. On allowing the liquid to evaporate spontaneously, a very good crystalline deposit of the nitrate remains, usually in the form of bold prisms. Crystals may be obtained in this manner from even a 1–10,000th solution of the alkaloid.

Potassium nitrate, as first observed by Mr. Bullock, throws down the same precipitate from solutions of jervine.

3. *Hydrochloric acid* produces in solutions of the alkaloid a white precipitate of the hydrochloride, which quickly becomes crystalline. The limit of the reaction of this acid is about the same as that of nitric acid.

The property of yielding precipitates with the foregoing mineral acids is highly characteristic of *jervine*.

4. *Ammonia* and the *fixed caustic alkalies* precipitate the alkaloid as a white deposit, which is insoluble even in large excess of the precipitant.

a. 1–100th grain yields a dense amorphous precipitate, which is soon changed into a mass of short, delicate needles.

b. 1–1000th grain: a rather copious precipitate, converted after a time into tufts of delicate needles.

c. 1–10,000th grain: soon long, delicate microscopic needles appear along the margin of the drop; after a time there is a well-marked precipitate.

The *alkali carbonates* produce the same precipitates as the free alkalies, only that the reactions are perhaps a little less delicate.

5. *Bromine in bromohydric acid* produces in solutions of the

alkaloid, even when highly dilute, a bright yellow, amorphous precipitate, which is readily soluble in alcohol.

6. *Platinic chloride* produces a deep yellow precipitate, even in solutions containing only 1–1000th of the alkaloid. After a time the precipitate becomes partly granular or crystalline. The precipitate is readily soluble in alcohol.

7. *Auric chloride* occasions a light yellow precipitate, which is readily soluble in alcohol. If the precipitate from 1–100th grain of the alkaloid be not agitated, it after a time becomes wholly converted into a mass of brush-like crystals. Crystals may be obtained under the reagent from 1–1000th grain of the alkaloid.

8. *Potassium sulphocyanide* produces in a 1–100th solution of jervine a copious, white, amorphous precipitate, which quickly assumes the crystalline form. 1–1000th solution yields a good crystalline precipitate.

9. *Potassium chromate* produces in a 1–100th solution a copious, yellow, amorphous precipitate, which after a time becomes converted into yellow nodular masses.

10. *Picric acid* throws down a yellow precipitate, which remains amorphous. The precipitate is produced in a 1–1000th solution of the alkaloid.

Separation from Organic Mixtures.

Veratrine may be separated from complex organic mixtures, as the contents of the stomach, and from the blood, in the same manner as already pointed out for the recovery of atropine from similar mixtures (see *ante*, 645). A portion of the residue thus obtained from the chloroform extract is examined by the sulphuric acid test, in the manner already indicated. Another portion may be heated with concentrated hydrochloric acid. Any remaining portion may then be dissolved in a small quantity of water containing a trace of acetic acid, and the solution, after filtration if necessary, examined by some of the liquid tests. Should the chloroform residue contain much foreign matter, it may be purified by dissolving it in acidulated water, rendering the filtered solution alkaline, and again extracting the liberated alkaloid by chloroform.

On examining, after this method, the contents of the stomach of the first cat heretofore mentioned, which had been killed in less than one minute by two grains of veratrine, and also of the young

dog, killed in two hours by three grains of the alkaloid, we in both instances recovered very notable quantities of the poison.

One fluid-ounce of *blood*, taken from the cat just mentioned, gave, when the chloroform residue was treated with sulphuric acid, very satisfactory evidence of the presence of the alkaloid. This case shows the great rapidity with which the poison may enter the circulation. The residue from six fluid-drachms of blood from the young dog, when examined by sulphuric acid, gave unequivocal evidence of the presence of the poison, the coloration being about as well marked as from any quantity of the pure alkaloid.

In poisoning by either Veratrum viride or Veratrum album, the *jervine* of the plant is more readily recovered from complex mixtures than the veratrine or amorphous alkaloids.

Experiments.—About one drachm of a fluid extract of Veratrum viride being given to a young cat, the animal was immediately rendered prostrate, and was dead in about *one minute* after the administration.

The *contents of the stomach* of the cat, with the finely-divided tissue of the organ, were strongly acidulated with acetic acid, the whole made liquid with water containing its own volume of alcohol, and the mixture digested at a moderate heat for half an hour. The strained liquid was then concentrated to a small volume, and filtered. The filtrate was treated with slight excess of sodium hydrate, and extracted by ether, which after separation was allowed to evaporate spontaneously.

The residue left by the ether contained a number of groups of crystals of *jervine*. The amorphous alkaloids were now removed from the residue by diluted hydrochloric acid, and the jervine further purified, when a very notable quantity of the crystallized alkaloid was obtained.

Seven fluid-drachms of *blood* taken from the cat were acidulated with acetic acid, and thoroughly agitated in a flask with about two volumes of diluted alcohol. The mixture was then digested for some time at a moderate heat, the liquid strained, then concentrated, and filtered. The filtrate, rendered alkaline, was then extracted by ether, which, after decantation, was allowed to evaporate, small portions at a time, in a small capsule.

Any jervine present in the residue thus obtained was very carefully dissolved in a little water strongly acidulated with acetic acid,

and the alkaloid again extracted from the alkalized filtered liquid by ether. The separated ether, on spontaneous evaporation, left an amorphous residue, which, on being moistened with diluted alcohol and spontaneous evaporation of the liquid, was almost wholly converted into crystals of the forms illustrated in Plate XIV., fig. 6. These crystals were found to consist of pure *jervine.*

In another experiment, jervine was recovered in its crystalline state from three ounces of *blood* taken from a dog that had swallowed between two and three drachms of the fluid extract of Veratrum viride, the animal having survived the effects of the poison two hours.

Of all the alkaloids, there is none, according to our experience, so readily recovered in its crystalline state from the blood, when carried to this fluid by absorption, as jervine.

Section II.—Solanine. (Nightshade.)

History.—Solanine, or *solania,* is the name given to a poisonous alkaloid found in *Solanum dulcamara,* or Woody nightshade, *Solanum nigrum,* or Garden nightshade, and in several other species of the Solanum genus of plants. It was first discovered, in 1821, by M. Desfosses, in the *Solanum nigrum.* Very different formulæ have been assigned to solanine, but, according to the more recent analyses of Zwenger and Kind, its composition is $C_{43}H_{71}NO_{16}$.

Preparation.—Solanine is most readily obtained, according to M. Wackenroder, from the apples of the common potato, *Solanum tuberosum.* The slightly crushed apples are covered in a suitable vessel for about fifteen hours with water containing sufficient sulphuric acid to give the mixture a strongly acid reaction. They are then expressed and removed, and the turbid acid liquid, with fresh portions of sulphuric acid, added to two successive quantities of fresh apples, and these macerated and removed as before. The liquid is now allowed to stand some days, then strained through linen, and treated with slight excess of powdered hydrate of calcium. After about twenty-four hours, the lime precipitate, containing the solanine, is collected on a linen strainer, dried in warm air, and boiled several times with successive portions of strong alcohol, which will extract the alkaloid. The united alcoholic extracts are then heated, and, while hot, filtered; on cooling, the liquid will deposit most of the alkaloid, partly in the form of crystalline laminæ and scales.

By dissolving ordinary solanine in water by the aid of hydrochloric acid, precipitating by ammonia, and frequent recrystallization from nearly absolute alcohol, Otto Gmelin obtained the alkaloid in the form of beautiful, colorless, silky needles of considerable length.

Some of the plants which owe their activity principally, if not entirely, to the presence of this alkaloid, have in several instances occasioned death; but we are not aware of any instance of poisoning in the human subject by the prepared alkaloid.

Symptoms.—*Solanum dulcamara*, or *Bittersweet*, when taken in an overdose, may give rise to dryness of the mouth and throat, thirst, nausea, headache, vertigo, vomiting, purging, and convulsions, followed in some instances by death. A little boy, aged four years, who had eaten at least two of the berries of this plant, was seized about fifteen hours afterward with purging and vomiting, and subsequently with convulsions, which continued during the day, leaving the child comatose and insensible during the intervals. Vomiting of bilious matters, having a dark-greenish color, continued, and during the evening the convulsions became permanent, and death ensued in about thirty-two hours after the poison had been taken. A sister of the deceased, aged six years, who had eaten only a single berry, was seized with sickness and purging, from which, however, she recovered without more serious effects. Another sister, still two years older, who had eaten two of the berries, escaped without any marked symptom. (*Lancet*, London, June, 1856, 715.) In two other cases, an unknown number of the berries proved fatal to two children. In an instance cited by Dr. Beck (*Med. Jur.*, ii. 825), several children who had eaten some of the berries were seized with violent pain in the intestines, vomiting and purging, and in one instance a profuse secretion of saliva. Under active treatment they all recovered.

So, also, the *Solanum nigrum* has in several instances destroyed life. Two little girls, between three and four years of age, ate a quantity of the leaves of this plant. Between two and three hours afterward they were both seized with pain in the bowels, vomiting, great uneasiness, picking at the bedclothes, and delirium. On the succeeding day, one of the children, who had suffered for several days from relaxed bowels, presented the following symptoms: the abdomen was much swollen, the pulse very frequent and scarcely perceptible; the respiration was quiet, the face pale, the pupils

strongly dilated, and there was great uneasiness of the body, picking at the bedclothes, and entire loss of consciousness. Notwithstanding active treatment, the child died, under extreme exhaustion, during the evening of the same day. The other child entirely recovered on the second day. (*Med.-Chir. Rev.*, Am. ed., Oct. 1860, 380.)

In an instance quoted by Orfila (*Toxicologie*, 1852, i. 313), three children who had eaten the berries of the garden nightshade were seized with severe headache, nausea, vertigo, colic, tenesmus, and copious vomiting. In one of the children, these symptoms were succeeded by extreme dilatation of the pupils, impaired vision, flushed face, profuse sweating, intense thirst, loss of voice, stertorous breathing, and tetanic convulsions, followed by death in about twelve hours after the berries had been eaten. The two other children, after suffering much the same symptoms, almost entirely recovered; but they had a relapse, under which they finally sunk.

Mr. Morris, of Merford, has related an instance in which a young girl, aged fourteen years, died from the effects of eating the berries of the *Solanum tuberosum*, or common potato plant. The symptoms described were great jactitation, lividity of the skin, cold and clammy perspiration, hurried respiration, and exceedingly quick and feeble pulse; the teeth for the most part were closed, and the patient was constantly spitting through the closed teeth a viscid frothy phlegm. There was also loss of speech; the tongue was covered with a dark brown moist fur; the expression was anxious, and the patient was extremely restless. Death took place on the second day. (*Med.-Chir. Rev.*, Oct. 1859, 389.) Dr. Christison quotes an instance in which four persons were seized with vomiting, insensibility, and convulsions after eating potatoes which had begun to germinate and shrivel. In sprouted potatoes, according to O. Bach, solanine exists only in the *peel* and that part of the tuber from which the shoot arises.

Solanine, in its pure state, seems to be much less potent in its effects than most of the alkaloids heretofore considered. In a series of experiments instituted by M. Schroff, and cited by Dr. Stillé (*Mat. Med.*, i. 763), with this substance, administered to healthy individuals in doses varying from one-thirtieth of a grain to three grains, he observed increased cutaneous sensibility, itching of the skin, gaping, general numbness, sleepiness, slight tonic cramps in the legs, and increased frequency of the pulse, which at the same time

grew feeble and thready; there was also some dyspnœa and oppression in breathing, with nausea and unsuccessful efforts to vomit; the head was hot, heavy, and dizzy, with drowsiness, yet with inability to sleep; the extremities were cold, the skin dry and itching, and there was marked general debility: the pupil remained unchanged.

Treatment.—The treatment in poisoning by solanine, or any of the plants that owe their activity to its presence, would consist in the speedy removal of the poison from the stomach by an emetic or the use of the stomach-pump. Vegetable infusions containing tannic acid, and stimulants, might be found useful.

Post-mortem Appearances.—In regard to the morbid changes produced by this substance, we are not acquainted with any instance in which they have been observed in the human subject.

Chemical Properties.

In the Solid State.—*Solanine*, when perfectly pure, may be obtained in the form of beautiful tufts of colorless, delicate, crystalline needles. As usually met with in the shops, it has a more or less yellow color, and occurs either in the form of an amorphous powder or as crystalline scales and granules. The pure alkaloid is destitute of odor, and has a bitter taste, followed by an acrid sensation in the throat. When gradually heated on porcelain, it fuses, then turns black, gives off dense white fumes, and leaves a solid carbonaceous residue; when heated in a direct flame, it readily takes fire, and is quickly consumed. According to A. Helwig, solanine may be sublimed unchanged, forming delicate needles.

Although having only a feeble alkaline reaction, solanine readily combines with acids, forming salts, several of which have been obtained in the crystalline state. The uncrystallizable salts usually appear in the form of transparent, colorless, gum-like masses. The salts of solanine are odorless, and have the bitter, acrid taste of the pure alkaloid.

Cold concentrated *sulphuric acid*, when brought in contact with pure solanine, immediately causes it to assume an orange-brown color, and slowly dissolves it to an orange-yellow solution; if the solution be heated, its color is quickly changed to deep dark brown. Concentrated *nitric acid* readily dissolves the alkaloid to a colorless solution, which after a time acquires a rose-red tint. This color is

developed in considerable intensity, if only a drop of the acid be employed, from the 1–100th of a grain of the alkaloid; but with the 1–500th of a grain the color is only just perceptible. If the nitric acid solution be heated, it acquires a faint yellow color. So, also, *hydrochloric acid* dissolves it without change of color; under the action of heat the solution throws down a white, flocculent precipitate.

If solanine be heated for some time with diluted sulphuric or hydrochloric acid, as first observed by MM. Zwenger and Kind, it is resolved into grape-sugar and a new, strongly basic alkaloid, which these observers named *solanidine*, and which, especially as the mixture cools, is deposited in combination with the acid employed in the crystalline form. (*Chem. Gazette*, xvii. 308.) According to O. Gmelin, this decomposition takes place with diluted sulphuric acid at a temperature of 50° C. (122° F.). A. Hilger assigned to solanidine the formula $C_{26}H_{41}NO_2$.

Solubility.—When excess of finely-powdered solanine is digested in pure *water* at the ordinary temperature, with frequent agitation, for several hours, one part dissolves in 1750 parts of the menstruum. The alkaloid is freely soluble in *alcohol*, which on slow evaporation leaves it principally in the form of delicate, silky, crystalline needles, Plate XIII., fig. 5. It is only very sparingly soluble in *absolute ether*, and almost wholly insoluble in *chloroform*, requiring about 9000 parts of the former, and not less than 50,000 parts of the latter liquid for solution. *Amyl alcohol*, when frequently agitated with excess of the powdered alkaloid for several hours, dissolves one part in 1060 parts of the liquid.

It is thus obvious that solanine cannot be extracted in very notable quantity from aqueous mixtures, either by ether or chloroform. From mixtures of this kind, however, the alkaloid may be separated by hot amyl alcohol, or, better still, by a mixture of ether and alcohol, in which mixture it is rather freely soluble. Thus, when 10–100ths of a grain of the alkaloid, in the form of sulphate, were dissolved in thirty grains of water, and the solution, after the addition of slight excess of potassium hydrate, agitated with five volumes of a mixture of two parts of absolute ether and one part of pure alcohol, the mixture extracted 9–100ths of a grain of the pure alkaloid, which on spontaneous evaporation it left in the crystalline form.

The *salts* of solanine are, for the most part, readily soluble in water; but they are insoluble in chloroform and in ether. Either of the latter liquids, therefore, may be employed to separate foreign organic matter from aqueous solutions of salts of the alkaloid.

Of Solutions of Solanine.—In the following investigations, in regard to the behavior of solutions of solanine, a sample of colorless crystallized solanine prepared by E. Merck, of Darmstadt, and a purified specimen of the commercial alkaloid, were employed, the former being dissolved in the form of sulphate, and the latter as chloride. Merck's preparation was in the form of delicate crystalline needles and thin transparent laminæ. The fractions employed indicate the fractional part of a grain of the anhydrous alkaloid present in one grain of water; and the results, unless otherwise indicated, refer to the behavior of one grain of the solution. One grain of a 1–100th aqueous solution of solanine in the form of sulphate, when allowed to evaporate spontaneously, deposits the alkaloidal salt chiefly in the form of groups of delicate acicular crystals, Plate XIII., fig. 6.

1. *The Alkalies and Alkali Carbonates.*

The *caustic alkalies* and their *monocarbonates* throw down from concentrated solutions of salts of solanine a colorless, transparent, gelatinous precipitate of the free alkaloid, which is readily soluble in excess of the fixed caustic alkalies, but only sparingly soluble in ammonia, and nearly wholly insoluble in the alkali carbonates. The precipitate is readily soluble in free diluted acids.

1. $\frac{1}{100}$ grain of solanine, in one grain of water, when treated with a small quantity of either of the above reagents, yields a nearly solid gelatinous mass.
2. $\frac{1}{500}$ grain, when treated with a small quantity of *ammonia*, yields a very good flocculent precipitate. On account of the ready solubility of solanine in the fixed caustic alkalies, it is difficult to obtain a precipitate by these reagents from a single drop of a 1–500th solution of the alkaloid.
3. $\frac{1}{1000}$ grain; under the action of a trace of ammonia, the mixture becomes very distinctly turbid, and after a time yields a distinct precipitate.

The true nature of the precipitate produced by either of these reagents may be established by the following test.

2. *Sulphuric Acid.*

If a small quantity of solanine or of any of its colorless salts, in the dry state, be treated with a few drops of cold concentrated sulphuric acid, the deposit immediately assumes an orange-brown color, and slowly dissolves to a yellow or orange-yellow solution, which after about an hour acquires a purplish-brown color and throws down a brownish precipitate; after several hours, the solution becomes colorless and the precipitate assumes a yellowish or dirty-white color. The intensity of the colors thus produced and the time of their development depend somewhat upon the quantity of the alkaloid present. Results similar to those just stated are obtained when a drop of a somewhat concentrated solution of a salt of the alkaloid is treated with several drops of the acid.

These results are principally due, according to Zwenger and Kind, to the *solanidine* produced from the solanine by the action of the acid. On treating different samples of *solanine* with concentrated sulphuric acid, we have frequently observed the peculiar nauseous odor first noticed by Wackenroder. When a solution of solanine sulphate is evaporated to dryness on a water-bath, the salt is left in the form of a hard, transparent, vitreous mass, destitute of any distinct crystalline structure.

1. $\frac{1}{100}$ grain of solanine, in the form of a salt, in the dry state, when treated with a few drops of the concentrated acid, soon dissolves, with an orange color, to a yellow solution, from which a precipitate soon begins to separate; this increases in quantity, and after a time the liquid acquires a deep orange, then a bright red, and finally a violet-pink color, which slowly fades, and after about ten hours entirely disappears.

   When one drop of a solution containing the 1–100th of a grain of the alkaloid is treated with several drops of the acid, the mixture immediately assumes a yellow color, and then passes through the changes just described.

2. $\frac{1}{1000}$ grain, both in the solid state and when in solution, yields much the same results as the preceding quantity of the alkaloid, only that the colors are less intense and persistent.

3. $\frac{1}{10,000}$ grain: when the dry deposit is touched with a small drop of the acid, it assumes a brownish color and dissolves to a solu-

tion having a decided yellow tint, which after a time changes to a very faint reddish hue.

4. $\frac{1}{50,000}$ grain, under the conditions just stated, dissolves with a just perceptible brownish tint to a colorless solution.

The production of this series of colors, in connection with the formation of the precipitate, is quite characteristic of solanine. Even the 1–1000th of a grain of the alkaloid, as just pointed out, will yield very satisfactory results.

If a little solanine be treated with a few drops of a warm mixture of equal volumes of concentrated *sulphuric acid* and *alcohol*, as first observed by Dr. Helwig, a beautiful *rose-red color* is quickly developed; this color may remain unchanged for several hours. Even a very minute quantity of the alkaloid will manifest this coloration. This reaction is not interfered with by the presence of morphine, even in relatively large quantity.

3. *Iodine in Potassium Iodide.*

An aqueous solution of potassium iodide containing free iodine causes somewhat concentrated solutions of salts of solanine to assume a deep orange-red color, and throws down an orange-brown precipitate, which is unaffected by diluted acids.

1. $\frac{1}{100}$ grain of solanine, in solution in one grain of water, yields the results just stated. The precipitate is readily soluble in potassium hydrate to a colorless solution, from which after a time a dirty-white precipitate separates.
2. $\frac{1}{1000}$ grain: an orange-brown solution and a slight precipitate.
3. $\frac{1}{5000}$ grain: the mixture assumes a yellowish-brown color, but fails to yield a precipitate.

The reactions of the first two mentioned solutions are peculiar to solanine; but with more dilute solutions the results are uncertain, since the reagent itself imparts a more or less yellowish-brown color even to pure water. It must also be borne in mind that the reagent produces reddish-brown precipitates with most of the other alkaloids and with certain other organic substances.

4. *Potassium Chromate.*

This reagent produces in solutions of salts of solanine, when not too dilute, a yellow, amorphous precipitate, which is insoluble in excess of the precipitant, but readily soluble in acetic acid. If the

mixture containing the deposit be treated with several drops of concentrated sulphuric acid, the precipitate quickly dissolves, and the solution slowly acquires a bluish or bluish-green color, which remains unchanged for several hours. The production of this color is peculiar to the precipitate produced from solutions of solanine.

1. $\frac{1}{100}$ grain of solanine, in one grain of water, yields a very copious precipitate, which, when treated with sulphuric acid, undergoes the changes just described.
2. $\frac{1}{1000}$ grain: the mixture immediately becomes turbid, and after a little time yields a quite fair, yellow, flocculent precipitate. If the precipitate be dissolved in a few drops of sulphuric acid, the solution soon acquires a quite distinct bluish-green color.
3. $\frac{1}{5000}$ grain: after a time a slight deposit of yellowish flakes.

Potassium dichromate produces much the same reactions as the monochromate, but the precipitate does not appear in quite as dilute solutions, since it is somewhat soluble in the chromic acid eliminated by the reaction when this reagent is employed.

5. *Bromine in Bromohydric Acid.*

An aqueous solution of bromohydric acid saturated with free bromine throws down from solutions of solanine salts an orange-yellow or yellow, amorphous precipitate, which is sparingly soluble in diluted acetic acid. After a time the precipitate acquires a dirty-white color, and slowly disappears.

1. $\frac{1}{100}$ grain of solanine, in one grain of water, yields a very copious orange-yellow precipitate.
2. $\frac{1}{1000}$ grain: a quite good, yellow deposit.
3. $\frac{1}{5000}$ grain yields only a just perceptible turbidity.

The reaction of this reagent is common to solutions of various other organic substances besides solanine.

Other Reagents.—Picric acid produces in concentrated solutions of salts of solanine a copious, yellow, gelatinous precipitate, which is readily soluble in excess of the precipitant. *Tannic acid* occasions a white, flocculent precipitate. *Ammonium oxalate* and *sodium phosphate* produce, in similar solutions, white, gelatinous precipitates.

Neither of the following reagents produces a precipitate, even in concentrated solutions of salts of the alkaloid: potassium sulpho-

cyanide, potassium ferro- and ferri-cyanide, the chlorides of gold, platinum, and palladium, potassium iodide, and free chromic acid.

Separation from Organic Mixtures.

Although there is no difficulty in identifying even a minute trace of solanine when in its pure state, yet when present in only minute quantity in complex organic mixtures its separation in a state sufficiently pure for testing is attended with considerable difficulty, and is sometimes impossible, at least by any method at present known. As the alkaloid is nearly wholly insoluble both in ether and in chloroform, it is obvious, as heretofore stated, that neither of these liquids will serve to separate it from organic mixtures.

The suspected mixture, as the contents of the stomach, after being carefully examined for the presence of any solid portions of the poisonous plant, is very slightly acidulated with a drop or two of sulphuric acid, and gently heated with diluted alcohol for about half an hour. The mass is then allowed to cool, transferred to a linen strainer, and the strained liquid concentrated on a water-bath to a small volume, after which it is filtered. The filtrate is evaporated, at a temperature not exceeding 49° C. (120° F.), to almost dryness, the residue well stirred with a small quantity of pure water, and the solution filtered. Any solanine present will now exist in the filtrate in the form of sulphate, and may, if not in too minute quantity, be separated by either of the following methods, the first of which is based upon the principles first applied by Wackenroder for the preparation of the alkaloid, and the second upon those first announced by Uslar and Erdmann.

According to the first of these methods, the clear filtrate is treated with slight excess of powdered calcium hydrate, and the mixture allowed to repose in a cool place for from twelve to twenty-four hours, in order that the eliminated solanine may completely subside. The precipitate is then collected on a filter and allowed to drain, then washed with a small quantity of cold water containing a trace of ammonium carbonate, and, while still moist, gently warmed with about half an ounce of strong alcohol, which will dissolve the alkaloid, whilst the calcium sulphate and any excess of caustic lime employed will remain, being insoluble in this liquid. The alcoholic solution, after filtration, is gently evaporated to dryness, the residue treated with a small quantity of water very slightly acidulated with

acetic acid, and the solution filtered. A drop of the filtrate may now be examined by the sulphuric acid test, and, if it yields satisfactory evidence of the presence of solanine, other portions of the solution by some of the other tests for the alkaloid. Should, however, the sulphuric acid test fail, the filtrate is concentrated and another drop examined in the same manner before applying any of the other tests.

Or, secondly, the filtrate, supposed to contain the sulphate of solanine, may be agitated with an equal volume of warm *amyl alcohol*, which, after the liquids have completely separated, is decanted, and the operation repeated with a fresh portion of the alcohol. By this treatment much of the coloring matter will be removed, while the alkaloidal salt will remain in the aqueous solution. This solution is then treated with slight excess of ammonium carbonate, and agitated with hot amyl alcohol, which will now dissolve the liberated alkaloid. The alcoholic solution is decanted, the aqueous liquid washed with a fresh portion of the hot alcohol, and the mixed alcohols evaporated to dryness on a water-bath. The residue is stirred with strong, ordinary alcohol, the solution filtered and evaporated to dryness. The residue thus obtained is treated with a small quantity of water containing a trace of acetic acid, and the filtered solution examined in the manner above described.

On following the methods now considered, for the examination of complex organic mixtures each containing two drachms of Thayer's fluid extract of dulcamara,—the medicinal dose of which is from half a drachm to one drachm,—we recovered by each a very notable quantity of solanine, in its very nearly pure state, especially when precipitated from the final aqueous solution by an alkali. The first-mentioned method furnished somewhat the best results; however, the quantity of the alkaloid recovered by either process was several times more than sufficient to establish fully the presence of the poison.

CHAPTER VI.

Gelsemine. Gelsemic Acid. (Yellow Jessamine.)

History.—*Gelsemine*, or *gelsemia*, is the active principle of *Gelsemium sempervirens*, popularly known as *yellow jasmine*. Gelsemine was first obtained in its pure state, and examined chemically, by the author, in 1870. (*Amer. Jour. Pharm.*, xlii. 1.) At the same time it was shown that the plant contained a non-nitrogenized principle, having an acid reaction, which was named *gelseminic*, or *gelsemic*, acid. M. Sonnenschein has claimed that this latter principle is identical in composition and chemical properties with the glucoside *æsculin*, found in the bark of the horse-chestnut, and in certain other barks; but we have elsewhere shown that this claim is quite erroneous. (*Ibid.*, July, 1882.)

MM. Sonnenschein and Robbins assigned to *gelsemine* the composition $C_{11}H_{19}NO_2$; but, according to A. W. Gerrard, its formula is $C_{12}H_{14}NO_2$, and that of the hydrochloride $2C_{12}H_{14}NO_2$; HCl. (*Pharm. Record*, March, 1883, 67.)

Preparation.—The finely-powdered root of the plant is thoroughly extracted with a mixture of equal volumes of strong alcohol and water, and the clear liquid concentrated at a moderate heat to a volume something less than the weight of the root employed. The liquid is then allowed to stand until the resinous matter has deposited, after which it is filtered. The filtrate is treated with slight excess of ammonia, and thoroughly agitated with something more than its volume of rectified ether, which will readily take up both the gelsemic acid and the alkaloid. The ether is decanted, and the extraction repeated two or three times with fresh portions of ether.

a. Gelsemine.—The ether thus employed is treated with slight excess of hydrochloric acid, added drop by drop, and the mixture allowed to stand some hours. The alkaloid will thus be precipitated

in the form of the hydrochloride, more or less granular and crystalline, and adherent to the sides of the vessel. After decanting the ether, the residue is washed with a little fresh ether, then dissolved in just sufficient water, and the filtered solution treated with slight excess of ammonia, which will precipitate the greater portion of the alkaloid as a pure white, curdy mass. This is quickly collected on a filter, washed with a little cold water, and allowed to dry.

To recover the gelsemine still remaining in the foregoing filtrate, the latter is concentrated, first by a moderate heat, then spontaneously, when the alkaloid, displacing in part the ammonia of the ammonium chloride present, will separate chiefly in the form of bold groups of prismatic crystals of the hydrochloride of gelsemine, Plate XV., fig. 1. These may be washed with a mixture of alcohol and ether. If the concentration has been carried to dryness, the residue may be washed with a little water, to remove any ammonium chloride present.

b. Gelsemic Acid.—On evaporation of the ether from which the alkaloid was precipitated by hydrochloric acid, the organic acid will be left in the form of comparatively large tufts and groups of crystals, Plate XV., fig. 2. These are washed with a little absolute alcohol, which will readily dissolve, in part at least, any coloring matter present. The crystals, if still colored, may be further purified by dissolving them in hot alcohol, which on cooling will deposit the excess in the form of delicate colorless needles.

From the dried root of the plant we have obtained, as the average of several different methods employed, about 0.25 per cent. of gelsemine and 0.5 per cent. of gelsemic acid. These principles seem to be present only in the bark of the root, the woody portion being entirely free.

Physiological Effects.—*Gelsemine* is an exceedingly active poison. One-eighth of a grain of the alkaloid being administered hypodermically to a cat, the animal soon exhibited signs of great distress, and in forty minutes there was great prostration, with difficulty in moving, the legs giving way, and the movements being frequently backwards. The respiration became greatly reduced, the pupils dilated to their fullest extent, and death took place in one hour and a half after the poison had been administered.

One-third of a grain of the alkaloid administered subcutaneously to a rabbit produced within ten minutes great weakness, then tremors of the body, backward movements, violent clonic convulsions in

which the animal turned a complete backward somersault; followed by gasping respiration and death within twenty-two minutes after the administration. A like quantity administered to a frog produced similar symptoms, with falling of the jaw and death in twenty minutes.

Two grains of *gelsemic acid* administered subcutaneously to a large rabbit produced no marked effect whatever. So, also, one-fifth of a grain produced no effect upon a pigeon. But one-half grain of the acid being administered hypodermically to a frog, quickly produced deep fluorescence of the eyes, great agitation, general prostration, and death in forty minutes. In another experiment, a like quantity of the acid caused a complete cataleptic condition and death within ten minutes. Repeated experiments with varying quantities of gelsemic acid indicated it to be very poisonous to frogs. These results confirm those previously obtained by Dr. J. Ott.

Gelsemium Preparations.—The preparations of gelsemium at present officinal are the *fluid extract*, one hundred parts of which represent one hundred parts of the *dried root;* and the *tincture*, one hundred parts of which correspond to fifteen parts of the root. The medicinal dose of the former preparation is from two to four minims; that of the latter, from fifteen to twenty-five minims.

The only preparation of the drug officinal prior to the *United States Pharmacopœia* of 1880 was the fluid extract, each fluid-ounce of which represented 480 grains of the dried root. The tincture then found in the shops had usually one-fourth, but sometimes only one-eighth, the strength of the fluid extract. A *concentrated* tincture representing 480 grains of the *fresh* root per fluid-ounce was also employed.

The present fluid extract is five per cent. *weaker* than that formerly directed. In a series of examinations of various samples of the fluid extract as formerly prepared, we found it to contain quite uniformly about 0.2 per cent. of gelsemine and 0.4 per cent. of gelsemic acid.

Poisoning by gelsemium preparations has of late years been of not unfrequent occurrence, but chiefly as the result of accident or ignorance, there being, so far as we know, only two or perhaps three cases in which it was criminally administered.

Symptoms.—The symptoms produced by poisonous doses of gelsemium are impaired sight, double vision, and sometimes total

blindness, with falling and loss of control of the upper eyelids; the face is congested, and the lips livid, but the face may be pale. The pupils are dilated, and usually insensible to light; the eyes fixed and more or less staring. There may be falling of the lower jaw, the mouth being sometimes wide open. Speech is impaired or entirely lost, and the tongue appears thick. The gait is staggering; the skin warm and moist, with occasionally free perspiration. The pulse is small, feeble, irregular, and intermittent, but it has been observed full and strong. There is great muscular relaxation, with general prostration and diminished sensibility, and the extremities are cold. The breathing is slow, labored, spasmodic, and sometimes stertorous. Violent spasms of the throat, resembling those of hydrophobia, have been present in a few cases. The mind usually remains clear, but unconsciousness has been present even when recovery followed.

The *time* within which the symptoms first appear has varied from a few minutes to about two hours, but they usually manifest themselves within half an hour. In a case related by Dr. W. W. Seymour, in which a teaspoonful of the fluid extract of gelsemium was given to a lying-in woman in mistake for ergot, *ten minutes* afterward she was extremely prostrated, almost pulseless, and the respiration was failing. She finally recovered. (*Boston Med. and Surg. Jour.*, Dec. 1881, 590.) Dr. R. P. Davis reports a case in which a delicate man, having taken a tablespoonful of Tilden's fluid extract of gelsemium, was found soon after lying upon his left side, the face somewhat congested, the pupils dilated, but responding to light; eyelids half closed, with inability to move them; the lower jaw drooping, and the tongue thick; his skin was warm and moist; the pulse small and feeble, and the respirations diminished in number. An emetic being administered failed to act. A little later, the patient was totally unconscious, the pupils widely dilated, the breathing spasmodic, the surface cold and congested; pulse almost imperceptible, and death took place in two hours and a half after the poison had been taken. (*Amer. Jour. Med. Sci.*, Jan. 1867, 271.)

In a case reported by Dr. J. E. Blake (*New York Med. Jour.*, April, 1875), a strong man took, by mistake, about two drachms of the tincture of the plant. Besides the usual effects, such as dimness of vision, prostration, diminished action of the heart and respiratory

organs, the patient, about half an hour after taking the dose, had symptoms closely resembling those observed in the frightful spasms of hydrophobia. At short intervals the most distressing paroxysms of dyspnœa occurred, during which he both clutched at his throat and beat the air with his hands. He finally recovered, being much relieved by morphia hypodermically administered. In another instance, related by Dr. J. T. Boutelle (*Boston Med. and Surg. Jour.*, Oct. 1874, 321), a young man, aged twenty-four years, suffering from neuralgia, took at 1 A.M. a teaspoonful of the fluid extract, and in fifteen minutes repeated the dose. The pain was soon relieved, and his eyes felt heavy, and in about half an hour he complained of choking, and soon arose struggling for breath, pushing his fingers into his throat, as if trying to tear it open. He staggered, as if intoxicated, threw himself upon the floor, and became unconscious. At 4 A.M. the respirations were gasping, the pulse was rapid and feeble, and the patient could not be roused. The pupils were dilated and insensible to light; the body was relaxed, the lower jaw drooping, the skin moist, the extremities cold, and, the pulse becoming slower and weaker, death took place at 4.45 A.M.

We have elsewhere reported a case in which three teaspoonfuls of the fluid extract were administered to a young, healthy married woman, several weeks advanced in pregnancy. In two hours after taking the dose, she complained of pain in the stomach, nausea, and dimness of vision. These symptoms were soon followed by great restlessness, ineffectual efforts to vomit, and free perspiration over the body. After five hours, the pulse was feeble, irregular, and intermittent; there was great prostration, with irregular and slow breathing, and the skin was dry. The extremities were cold, the pupils dilated and insensible to light; the eyes were fixed, and control over the eyelids was lost. The vital powers rapidly gave way, and death occurred in seven hours and a half after the poison had been taken. (*Amer. Jour. Pharm.*, Jan. 1870, 14.)

Period when Fatal.—Of twenty-five cases of gelsemium poisoning that we have collected, thirteen proved fatal, and the fatal period varied from *one hour* to *seven hours and a half*. In a case communicated to me by Dr. M. P. Hatfield, of Chicago, fifteen grains of the resinoid "gelsemin" proved fatal to a woman in *one hour*. The three following cases are briefly related by Dr. J. N. Freeman, of Brooklyn. (*Lancet*, Sept. 1873, 475.) A boy, three years old, took,

by mistake, about fifteen minims of tincture of gelsemium (made by macerating four ounces of the root in a pint of dilute alcohol), and died from its effects in *two hours*. The first symptoms noticed were double vision and a staggering gait, soon followed by complete muscular relaxation. In the second case, a girl, aged nine years, took a dessertspoonful of the tincture. Soon after taking the dose, she complained of dimness of sight, double vision, and loss of muscular power, and died in *less than two hours*. In the third case, a boy, about three years old, was ordered every two hours a teaspoonful of a mixture containing ten grains of sulphate of quinine, one drachm of tincture of gelsemium, and five drachms of syrup. After the first dose he became prostrated, and staggered in walking; but in due time the dose was repeated. About half an hour after taking the second dose the body was perfectly flaccid, the pupils were dilated, there was froth at the mouth, the heart was beating feebly and slowly, and the pulse was imperceptible at the wrist. Death took place half an hour later.

In a case reported by Dr. W. W. Seymour, a strong man, aged twenty-eight years, took a quantity of the tincture, variously stated from three drachms to two ounces, and died from its effects, under the usual symptoms, in *six hours* after the physician was called. (*Boston Med. and Surg. Jour.*, Dec. 1881, 590.)

Fatal Quantity.—At present it is impossible to indicate the least fatal quantity of this drug. Prof. Seymour, of Troy, states that he has seen repeated instances in which *two minims* of the fluid extract, given three times a day, affected the sight; and four minims, three times a day, produced weakness of the legs and staggering. In a case reported by Dr. Freeman, cited above, a quantity of the tincture equivalent to about *twelve minims* of the fluid extract proved fatal to a boy, aged three years. And a case is related in which thirty-five drops of a tincture of the drug caused death in one hour and a half. A physician took, as we are privately informed, a mixture containing fifteen minims of the fluid extract, and repeated the dose at short intervals. After the fourth dose the usual symptoms of the poison appeared, and terminated fatally in less than four hours. In another instance, a physician, suffering from facial neuralgia, took *ten minims* of the fluid extract, and repeated the dose in half an hour. In fifteen minutes after the second dose there was great drowsiness, and pain over the frontal region; the pulse was weak and intermittent, the body cold and shivering; the pupils were

slightly contracted, and there was a general feeling of collapse. After vomiting freely, the patient rapidly recovered. (*Med. Times*, March, 1881, 382.)

In a case mentioned by Dr. Seymour, a teaspoonful of the fluid extract proved fatal to a young lady. And in a case already cited, two teaspoonfuls of the fluid extract, given in divided doses, proved fatal to a young man in less than four hours. Half a teaspoonful of a preparation of gelsemium, being given to each of two children, was soon followed by the ordinary symptoms, and death in less than three hours. (*Eclectic Med. Jour.*, May, 1879, 222.) Dr. A. L. Hall reports a case (*Med. Record*, Jan. 1882, 65) in which a strong woman took eight grains of "gelsemin," in two-grain doses repeated every three hours, and died from its effects within an hour after taking the last dose. The same writer cites three other instances in which two, three, and four grains respectively of the same preparation produced very alarming symptoms.

The following cases of *recovery* may be mentioned. A lady took, by mistake, a teaspoonful of the fluid extract. Dimness of vision came on in an hour, and was followed by paralysis of the muscles of the lower jaw and tingling of the extremities. Five and a half hours later, she believed herself to be dying. There was great difficulty in swallowing, faintness, and difficult articulation; the mouth was wide open; the pupils were greatly dilated, and insensible to light; the pulse was rapid and feeble. Under the administration of carbonate of ammonium, and the use of electricity, she slowly recovered. (Dr. F. W. Goss, *Boston Med. and Surg. Jour.*, July, 1879, 16.) In a case reported by Dr. R. P. Davis, a man recovered after taking a *teaspoonful* of the fluid extract. The treatment in this case consisted of an emetic, which acted freely, followed by large doses of quinine and brandy. (*Amer. Jour. Med. Sci.*, Jan. 1867, 271.)

TREATMENT.—No chemical antidote for this poison is yet known. The contents of the stomach should be evacuated as speedily as possible, and then internal and external stimulants employed. In several instances the application of electricity has been found very beneficial. A striking instance of this kind is reported by Dr. J. T. Main, who through mistake swallowed one drachm of the fluid extract of gelsemium. (*Boston Med. and Surg. Jour.*, April, 1869, 185.) After a time he became nearly blind; control over the eyelids was almost entirely lost; the flexor muscles of the

hands and arms were paralyzed, whilst the extensors were nearly so. Sensation in the hands and arms was blunted, but not in proportion to the loss of motion. The speech was somewhat affected, and a very disagreeable sensation was felt in the head, even before the muscles came under the influence of the drug; but the mind was clear. In this condition he requested the poles of a galvanic battery to be applied to his hands, which being done, he was instantly relieved. The relief was not only instantaneous, but perfect and permanent. Dr. Main states that he has since tried the same remedy upon persons pretty well under the influence of gelsemium, and with like beneficial results. In a case reported by Dr. Seymour, the application of electricity was attended with great relief at first, but the patient finally died.

The following remarkable case of recovery, in which *morphine* was employed, is reported by Dr. G. S. Courtright. (*Lancet and Observer*, Cincinnati, Nov. 1876, 961.) A physician took, by mistake, from one to two teaspoonfuls of the tincture of the drug. Within a few minutes his vision was affected, and he soon lost entire control over the movements of his head; the breathing was slow; the pulse rapid and feeble. The face was congested, the lips were livid, the muscles of the lower jaw and of the eyelids completely paralyzed, the pupils dilated, and the eyes fixed. Two hours after the poison was taken, an emetic having failed to act, about *three grains* of morphine were injected into the arm, in divided doses, within a few minutes, and half a grain was given internally. Very quickly there was some improvement in the breathing; the pupils became slightly contracted, the eyes less fixed, and there was slight control over the eyelids. Soon after, the patient vomited; the pulse became stronger and less frequent, the paralysis gradually subsided, and in two hours he was able to give an account of the accident. In Dr. Blake's case, already cited, the hypodermic use of morphine was attended with good results.

Post-mortem Appearances.—Nothing peculiar has been observed in the appearances after death from poisoning by this substance. In Dr. Boutelle's case, in which a teaspoonful of the extract proved fatal in less than four hours, the examination was made five and a half hours after death. The body was well nourished; rigor mortis marked. The blood was very fluid, of a dark color, and showed no tendency to coagulate or turn red upon exposure to the

air, even after standing some hours. The heart, lungs, spleen, and kidneys were normal. The liver was dark-colored and contained much liquid blood. The stomach contained four ounces of a light-colored fluid mixture mixed with glairy mucus. Its internal surface was deeply congested and marked by tortuous dilated vessels. The intestines were normal. The brain was rather pale, and the internal substance of the lobes was dotted here and there with small red points.

In the case we have elsewhere reported, the body eight days after death presented the following appearances, as observed by Dr. Stephenson. The countenance was natural; cadaveric rigidity very slight. The membranes and substance of the brain and medulla oblongata were normal. The adipose tissue was thick and highly tinged with bilious matter. The lungs were slightly collapsed, but natural in appearance, and the superficial veins were congested. The heart was normal in size, the external veins were injected, and the cavities greatly distended with dark grumous blood, inside of which was a well-defined membranous deposit. The stomach contained a small quantity of ingesta. The peritoneum, intestines, liver, and investing membrane were normal. The left kidney was congested.

The cases just cited are, so far as we know, the only ones in which the *internal* appearances in gelsemium poisoning have been observed. In Dr. Hall's case, soon after death, the external appearances were life-like. The skin was moist; the body warm, with slight coldness of the limbs; the eyelids were drooping, the pupils dilated; the lower jaw was relaxed, and the mouth presented an oval appearance.

Chemical Properties.

In poisoning by *gelsemium* preparations the chemical examination should be directed to the recovery of both *gelsemic acid* and *gelsemine*, especially as the acid exists in the larger quantity in the plant, and so readily reveals its presence by its fluorescent properties.

I. Gelsemic Acid.—In its pure state gelsemic acid is a colorless, odorless, nearly tasteless solid, which readily crystallizes, either in groups of prisms or tufts and single needles, or minute plates and scales. It has only a feeble acid reaction, and forms definite salts with but few of the metals. When gradually heated to about

163° C. (325° F.) it fuses to a clear liquid, which may be vaporized without change of color or composition. If the vapors be received on a warm glass slide, they condense to brilliant crystals of the forms illustrated in Plate XV., fig. 3. Crystals may also be obtained by heating a small portion of the acid in a reduction tube.

Solubility. In Water.—When excess of the finely-powdered acid is frequently agitated with water at the ordinary temperature for twenty-four hours, one part dissolves in 2912 parts of the liquid. Its solubility is greatly increased by the presence of coloring matters, and also of the associated alkaloid, even if only a trace of the latter be present. It is much more soluble in hot water, from which, however, as the solution cools the excess soon separates in delicate needles.

Gelsemic acid is readily soluble both in *ether* and in *chloroform*. In ether of sp. gr. .728, one part of the acid quickly dissolves in 300 parts of the fluid. It is freely soluble in *alcohol*.

Chemical Reactions.—1. *Nitric acid.*—If a small portion of gelsemic acid be treated with a drop of nitric acid, it dissolves with a yellow color to a yellow or reddish solution, the final color depending upon the relative quantity of the organic acid present. On treating this solution with excess of *ammonia*, it acquires a permanent deep or blood-red color. These results may be obtained from the 1–1000th of a grain of the acid; and even 1–50,000th grain will yield, under the action of ammonia, a marked reddish coloration.

This reaction, although exceedingly delicate, is not characteristic of gelsemic acid, since *æsculin* yields under the action of nitric acid and ammonia a similar red coloration. The distinctive characters of these substances will be pointed out hereafter.

2. *Sulphuric acid.*—Sulphuric acid slowly dissolves *pure* gelsemic acid under a yellow color to a yellow solution, which is unchanged by a moderate heat; even if the mixture be heated to 100° C. (212° F.) the acid is not decomposed. If the organic acid is impure, the cold sulphuric acid solution may have a reddish color, changed to deep brown by a moderate heat. *Æsculin*, when pure, *quickly* dissolves in sulphuric acid to a faintly yellow solution, which when moderately heated soon acquires a chocolate color, then becomes charred. If a small crystal of potassium dichromate be stirred in a sulphuric acid solution of gelsemic acid, green oxide of chromium quickly appears.

3. *Sulphuric acid and Ammonia.*—If a drop of aqueous ammonia be allowed to flow into a drop of a sulphuric acid solution of gelsemic acid, the latter immediately separates as a mass of crystalline needles, along the margin of contact of the two liquids. 1–1000th of a grain of the acid, under these conditions, will yield a very copious crystalline deposit, Plate. XV., fig. 4. And even 1–10,000th of a grain, if only a minute drop of the mineral acid be employed and excess of ammonia be avoided, will yield perfectly satisfactory results. These crystals may be repeatedly re-examined, even when only in minute quantity and after long periods, by treating the dry residue, after spontaneous evaporation, with a drop of water, which will readily dissolve the ammonium sulphate present, whilst the gelsemic acid crystals will remain.

This is one of the most delicate and characteristic reactions of gelsemic acid yet known, and it is not readily interfered with by the presence of foreign matter. Æsculin fails to respond to this test.

4. *Hydrochloric acid* fails to dissolve or act upon gelsemic acid, even when heated to 100° C. (212° F.). Æsculin is readily soluble in this acid.

5. *Ammonia*, and the *fixed caustic alkalies*, cause gelsemic acid to assume an intense yellow color, and quickly dissolve it to solutions having very striking fluorescent properties, even when greatly diluted. When the diluted solution is examined by transmitted light, it has a yellow color; under reflected light, a deep bluish appearance; and under condensed sunlight, an intense blue color along the path of the condensed rays. This fluorescence still manifests itself in solutions containing only 1–100,000th of the acid. It may also be observed, on addition of an alkali, in the commercial preparations of gelsemium. The fluorescence of gelsemic acid is quickly destroyed by free acids.

In regard to the fluorescent properties of gelsemic acid, it must be borne in mind that *æsculin* and certain other vegetable principles possess similar properties. The well-known fluorescence of quinine reveals itself only in the presence of a free acid, being quickly destroyed by an alkali.

Solutions of Gelsemic Acid.—In the presence of a free alkali, gelsemic acid is freely soluble in water, forming the fluorescent solutions just mentioned. From solutions in ammonia, when not too dilute, hydrochloric acid precipitates the acid in its crystalline

state, usually as delicate needles. In the presence of a fixed alkali, the acid is precipitated only from quite strong solutions.

If a drop of the ammoniacal solution be allowed to evaporate spontaneously, the acid is left in its *free* state, as prisms and needles. Crystals may thus be obtained from a drop of a 1–10,000th solution of the acid. The residue from a solution of the acid in a *fixed* alkali has a greenish-yellow color and is amorphous.

Solutions of the acid, prepared by the aid of just sufficient alkali, yield precipitates with solutions of most of the metals. In some instances these precipitates are definite compounds of the acid and metal; in others they are mixtures of the metallic oxide and free gelsemic acid; whilst in still others they are due to the reducing action of the acid.

1. *Acetate of lead* throws down from a 1–100th solution of gelsemic acid a dense, dirty-yellow, amorphous precipitate, which is readily soluble in acetic acid, but is soon replaced by delicate crystalline needles. A 1–1000th solution yields a very decided precipitate.

2. *Mercuric chloride*, or *corrosive sublimate*, produces with a 1–100th solution a copious, yellowish-white precipitate, from which the free acid quickly separates as tufts of crystals. Crystals may thus readily be obtained from even a drop of a 1–1000th solution of the acid.

3. *Silver nitrate* causes a brownish-yellow deposit, which soon darkens in color and finally becomes bluish-black, due to the reduction of the silver salt. Even a drop of a 1–50,000th solution of the acid after a time acquires a distinct purplish color.

4. *Copper sulphate* throws down from tolerably strong solutions of the acid a dirty-brown precipitate, which soon acquires a dull red color; after a time crystals of the free acid separate.

5. *Auric chloride* occasions with strong solutions a deep blue deposit, which soon assumes a green color.

None of the above liquid reactions when taken alone is characteristic of gelsemic acid. In cases, however, in which the acid separates in the crystalline state, its true nature may be determined by some of the preceding tests.

II. GELSEMINE.—In its pure state, *gelsemine* is a colorless, odorless, difficultly crystallizable solid, having a persistent bitter taste.

It has a strong alkaline reaction, and completely neutralizes acids, forming *salts*, most of which are readily soluble in water and in alcohol. The hydrochloride rather readily crystallizes in groups of prisms, Plate XV., fig. 1. The sulphate, nitrate, and hydrobromide may also be obtained in the crystalline form.

When heated, gelsemine fuses, according to Dr. Gerrard, at 45° C. (113° F.), to a colorless, viscid liquid, which on cooling solidifies to a transparent, vitreous mass. At a higher temperature, the alkaloid is dissipated without residue, in the form of white fumes, from which we failed to obtain crystals.

Solubility.—In its free state, gelsemine requires, at the ordinary temperature, 644 parts of *water* for solution, even when excess of the alkaloid is kept in contact with the fluid for many hours.

Gelsemine is freely soluble in *chloroform* and in *ether:* one part of the alkaloid is quickly dissolved by twenty-five parts of the latter liquid. It is also readily soluble in alcohol.

Reactions in the Solid State.—1. *Sulphuric acid.*—When a small portion of *pure* gelsemine is treated with a drop of sulphuric acid, it slowly dissolves, with little or no change of color, even when the solution is moderately heated. When, however, the alkaloid is not perfectly pure, it dissolves with a more or less reddish or brownish color to a solution which after a time assumes a pinkish hue, and which when heated acquires a purple or chocolate color.

If a minute portion of powdered *potassium dichromate* be slowly stirred in a sulphuric acid solution of gelsemine, or of any of its colorless salts, a beautiful *reddish-purple* or *cherry-red* color manifests itself, and the liquid quickly acquires a bluish-green or blue color. If only minute quantities of the acid and powder be employed, the 1–10,000th of a grain of the alkaloid will yield satisfactory results; and even the 1–100,000th of a grain may develop, at least, the reddish-purple coloration.

If, in this test, the dichromate of potassium be replaced by *ceric oxide, manganic oxide,* or *potassium ferricyanide,* similar results may be obtained. If the sulphuric acid solution of the alkaloid be heated on a water-bath for some minutes, it no longer responds to the color reaction of the oxidizing agent; but the alkaloid is not destroyed, since it may be recovered by neutralizing the solution with barium hydrate and extraction with ether.

This color reaction of gelsemine resembles somewhat that pro-

duced by strychnine, especially as obtained from very minute portions of the latter alkaloid. When, however, the strychnine reaction is well marked, the primary blue and rapid succession of colors readily distinguish it from gelsemine.

2. *Nitric acid.*—This acid dissolves perfectly pure gelsemine, and any of its colorless salts, with little or no color; but on spontaneous evaporation of the liquid, a permanent bluish-green stain is left on the porcelain, even if only a minute trace of the alkaloid be present. In the state in which gelsemine is usually obtained, especially as an ether or chloroform residue, nitric acid causes it to assume a yellowish or brownish-green color, which quickly changes to deep green. About the least visible quantity of the alkaloid, if quietly touched with a minute drop of the acid, may develop this green coloration in a marked degree.

Strychnine and the other alkaloids fail to yield a bluish-green or green coloration under the action of this acid. If the nitric acid residue from gelsemine be treated with a minute quantity of sulphuric acid and potassium dichromate, the reddish-purple coloration of the alkaloid will be developed. The nitric and sulphuric acid tests may thus be applied to the same portion of the alkaloid.

Hydrochloric acid readily dissolves gelsemine, if pure, to a colorless solution.

The caustic alkalies have little or no action upon the solid alkaloid.

Solutions of Gelsemine.—Solutions of the salts of gelsemine, when pure, are colorless, and have a bitter taste, which is still well marked in a drop of a 1–1000th solution of the alkaloid. On spontaneous evaporation of a drop of the hydrochloride solution, the salt may be left in its crystalline state.

1. *Ammonia* and the *fixed alkalies* precipitate gelsemine from tolerably strong solutions of its salts as a white, amorphous deposit, which after a time becomes more or less changed into minute granules and crystalline plates. The precipitate is somewhat soluble in excess of the precipitant. A drop of a 1–100th solution of the alkaloid yields a copious precipitate. If a strong solution be exposed to the *vapor* of ammonia, an immediate cloudiness is produced, followed by a granular deposit. In the residue from an aqueous mixture of a salt of gelsemine and excess of ammonia, as already stated, the alkaloid remains as a salt, the ammonia being displaced.

2. *Picric acid* produces in solutions of gelsemine salts a yellow,

amorphous precipitate. 1–100th of a grain of the alkaloid in one grain of water yields a very copious, bright yellow deposit; 1–1000th grain, a greenish-yellow precipitate.

3. *Iodine* in a solution of *potassium iodide* throws down from solutions of salts of gelsemine a brown, amorphous precipitate which is only sparingly soluble in acetic acid. The precipitate still appears in a drop of a 1–10,000th solution of the alkaloid.

4. *Bromine* in *bromohydric acid* causes a yellowish, amorphous precipitate, which still manifests itself in a 1–5000th solution of the alkaloid.

5. *Auric chloride* produces a yellow precipitate, which dissolves with difficulty in acetic acid. A few drops of a 1–1000th solution of a salt of the alkaloid yield a very marked precipitate, which quickly dissolves on heating the mixture and separates in the granular form as it cools. According to A. Gerrard, the precipitate has the composition $2C_{12}H_{14}NO_2$; $HCl,2AuCl_3$.

6. *Platinic chloride* occasions in tolerably strong solutions of gelsemine salts a light yellow precipitate, which becomes partly granular and is readily soluble on heating the mixture. Its composition is $2C_{12}H_{14}NO_2$; $HCl,PtCl_4$ (Gerrard).

7. *Mercuric chloride* throws down from strong solutions of the salts of the alkaloid a white precipitate, which is only sparingly soluble in hydrochloric acid. Comparatively large granules may sometimes be obtained from the precipitate.

8. *Potassium dichromate* produces in a 1–100th solution of a gelsemine salt a copious, yellow precipitate, which becomes somewhat granular. Solutions but little more dilute fail to yield a precipitate. Sulphuric acid causes the precipitate to assume a deep bluish-green color, and on stirring the mixture the characteristic purple coloration of the alkaloid is developed. If excess of the dichromate reagent be avoided and the liquid evaporated spontaneously, the residue from even the 1–10,000th of a grain of gelsemine will, when treated with sulphuric acid, yield a series of purple colorations followed by a bluish-green hue.

Similar color results may be obtained with sulphuric acid by employing *potassium ferricyanide* as the precipitant. This reagent, however, produces *precipitates* from only concentrated solutions of gelsemine salts.

It need hardly be stated that none of the foregoing liquid reac-

tions is in itself characteristic of gelsemine. But if the *precipitates* produced by any of the reagents be treated with concentrated sulphuric acid and potassium dichromate, or other color-developing agent, the peculiar purple coloration of gelsemine will be developed. It must be remembered, however, that the color reaction of some of these precipitates, especially when excess of the precipitant is present, is not so delicate as that of the free alkaloid or its pure salts.

Recovery from Organic Mixtures.

Suspected Solutions and Contents of the Stomach.—The mixture, diluted with water if necessary, is slightly acidulated with acetic or hydrochloric acid, and digested at a moderate heat on a water-bath for an hour or longer. The cooled liquid is strained through muslin, the solids washed with alcohol, and the united fluids concentrated to one or two fluid-ounces (30 to 60 c.c.), or even less if only a small portion of solid matter is present. The liquid is now filtered, and any solids on the filter washed with a mixture of equal parts of alcohol and water. It is again concentrated, taking care to expel the alcohol, allowed to cool, and, if solid matter separates, again filtered. The analysis now divides itself into two parts.

a. Gelsemic acid.—The liquid, having still an *acid* reaction, is agitated with about twice its volume of pure *ether*, which will take up any gelsemic acid present and become more or less fluorescent. After decanting the ether, the aqueous liquid is washed once or twice with small portions of fresh ether, which is collected with that first employed. The aqueous liquid is reserved for examination for the alkaloid.

The ether thus employed is allowed to evaporate spontaneously, small portions at a time, in a thin glass capsule. The gelsemic acid may now be found, especially in the margin of the deposit, in the form of groups or single needles, readily seen by a low power of the microscope. Any crystals thus obtained may be collected, and, if not in too minute quantity, washed with a few drops of absolute alcohol, then examined by the appropriate tests for the acid.

If much foreign matter is still present, the entire residue may be treated with a little water containing a drop of ammonia, and the liquid, if necessary, filtered. After examining the alkaline liquid in regard to its fluorescence, it is slightly acidulated with acetic acid and extracted with ether, which is allowed to evaporate spontane-

ously. A portion of the ether residue may be examined by the nitric acid and ammonia test for the organic acid. Another portion may be dissolved in a small drop of sulphuric acid, and then a minute drop of ammonia carefully added, when any gelsemic acid present will separate as very delicate needles. Both these tests may react with the gelsemic acid even in the presence of considerable foreign matter.

b. Gelsemine.—The acid aqueous liquid from which the gelsemic acid was extracted by ether is gently warmed until the dissolved ether has been expelled. It is then rendered slightly alkaline by ammonia or sodium carbonate, and any gelsemine present extracted by ether or chloroform in the usual manner.

Should the ether or chloroform residue be too impure for the satisfactory application of the tests, it is treated with a small quantity of water slightly acidulated with hydrochloric acid, and the filtered solution, rendered alkaline, again extracted with ether. Portions of the final residue should be examined by the sulphuric acid and potassium dichromate and the nitric acid tests for the alkaloid. It may be remarked that the reactions of these tests are more readily interfered with by the presence of foreign matter than those of the corresponding tests for gelsemic acid.

After the above general method, we have in several instances obtained very satisfactory evidence of the presence of both gelsemic acid and gelsemine in the stomach-contents of animals poisoned by small doses of gelsemium preparations. So, also, in the case already cited, in which three teaspoonfuls of the fluid extract proved fatal to a woman, very satisfactory evidence of the presence of the organic acid, and of the alkaloid in minute quantity, was obtained from the contents of the stomach *four and a half months* after death.

From the Tissues.—In gelsemium poisoning both gelsemic acid and gelsemine are absorbed, and enter the circulation in apparently the relative proportions in which they are present in the plant. The absorbed poison may be recovered from the *liver* by treating the finely-divided or crushed tissue with several times its weight of water slightly acidulated with hydrochloric acid, and gently warming the mixture on a water-bath for some hours, occasionally adding water to replace that evaporated. The cooled liquid is strained and the solids well washed with water. The clear liquid is concentrated at a moderate heat to a small volume, and, when cooled, filtered.

Any gelsemic acid present is now extracted from the still *acid* solution by ether in the manner already indicated; after which, the dissolved ether being expelled, the aqueous liquid is rendered slightly alkaline and the alkaloid extracted in a similar manner.

A cat which had been under the influence of the drug for fifteen hours was given two drachms of the fluid extract. The animal was immediately paralyzed, and was dead fifteen minutes later. The liver, on being examined after the above method, furnished groups of crystals of gelsemic acid, and very satisfactory evidence of the presence of gelsemine. Like satisfactory results were obtained from the liver of a rabbit killed by the drug.

From the Blood.—A few ounces of the blood are mixed with about five volumes of a mixture of equal parts of alcohol and water, a few drops of acetic or hydrochloric acid added, and the whole agitated in a bottle until a homogeneous mixture is formed. This is moderately heated in the closed bottle for some time in a water-bath, the mixture being frequently agitated. The cooled liquid is strained, and the solids washed with diluted alcohol and pressed. It is then concentrated at a moderate heat, filtered, and the filtrate evaporated to a thin syrup; this is extracted with water and the filtered liquid concentrated to a small volume.

From the liquid thus prepared the gelsemic acid and gelsemine are extracted by ether in the usual manner.

A fluid-ounce of blood taken from the cat mentioned above was examined after this method. The ether extract from the acid aqueous liquid presented a well-marked fluorescence, and on evaporation left tufts of crystalline needles of gelsemic acid; and a portion of the residue gave a deep red coloration with nitric acid and ammonia; whilst another portion, when treated with sulphuric acid and ammonia, gave a good deposit of crystalline needles. So, also, the ether extract from the *alkaline* liquid furnished very satisfactory evidence of the presence of gelsemine.

APPENDIX.

BLOOD.

COMPOSITION—DETECTION—DISCRIMINATION.

I. General Nature and Properties of Blood.

Physical Characters.—In its natural condition, the blood is a somewhat viscid, opaque liquid, of a characteristic red color, which is bright scarlet in arterial and of a purplish or brownish hue in venous blood. On exposure to the air the blood of the veins acquires the florid hue of that of the arteries. The blood has a feebly alkaline reaction, a saline taste, and, while still warm, a faint odor, which differs somewhat in the blood of different animals. Its average specific gravity in man is about 1055, ranging from 1045 to 1075, and being slightly lower in women than in men, and still lower in children. The specific gravity of the blood of domestic animals is about the same as that of man.

Composition.—When examined under the microscope, the blood is found to consist of a transparent, colorless, or very faintly yellow liquid, known as the *liquor sanguinis*, or *plasma*, in which is suspended a great number of very minute solid bodies known as the *blood-corpuscles.*

The *liquor sanguinis* consists chiefly of water holding in solution *albumen*, *fibrin*, *extractive matters*, and certain inorganic *salts*, of which the principal are sodium chloride and carbonate. The *corpuscles* are of two kinds: the *colored*, consisting largely of the red coloring substance, variously termed *hæmoglobin*, *hæmatoglobulin*, and *hæmatocrystallin*, which confers upon the blood its red color; and the *colorless*

or *white* corpuscles, these being destitute of color and present only in small proportion to the former.

These several components exist in about the following proportions in 1000 parts of human blood: water, 790; albumen, 65; fibrin, 3; extractive matters and salts, 17; corpuscles (dry), 125 parts. In their moist state, it is estimated that the corpuscles form about one-half the volume of the blood. The specific gravity of the red corpuscles, according to C. Schmidt, is about 1088, and that of the fluid in which they float about 1028. When seen singly, the red corpuscles have a pale reddish-yellow hue.

Coagulation.—Soon after being drawn from the body, the blood undergoes spontaneous *coagulation*, whereby it finally separates into two distinct portions, namely, the *crassamentum*, or *clot*, consisting of the *fibrin* with the *corpuscles* entangled in its meshes; and the *serum*, holding in solution the *albumen* and *saline* matters. This process usually begins in normal human blood, when exposed to the air, in from two to three minutes, and in about eight minutes the mass forms a jelly. It is, however, subject to considerable variation, and also varies in the blood of different animals.

According to Hewson, coagulation may take place within a few seconds, whilst it may be delayed for an hour or longer. (*Op. cit.*, 72.) As is well known, the process is much influenced by various conditions and agents. Thus, an increased temperature hastens, while a diminished temperature delays, coagulation. So, also, the addition of water up to four-tenths the volume of blood hastens, and a larger proportion retards, the process (Hasebrock, 1883). In like manner a minute quantity of sodium chloride hastens, and a large quantity prevents, coagulation.

Corpuscles.—The existence of the blood-corpuscles was first announced by Malpighi, in 1661, he having observed them in the blood of the hedgehog. They were first seen in human blood by Leeuwenhoek, in 1664, and he observed that the red color of the blood resided in the corpuscles, and, as in man, they were circular in outline in the blood of the rabbit, ox, and sheep, but oval in birds, fish, and the frog. (*Watt's Dict. Chem.*, i. 604.) Swammerdam was the first to observe the blood-corpuscles of the frog. The earlier observers believed the corpuscles to be globular in form, but Senac, in 1749, announced that they were all more or less flattened.

Number.—According to Vierordt, and also Welcker, one cubic

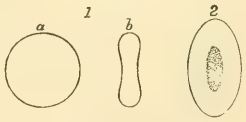
millimetre (about 1–25th inch linear) of normal human blood contains about 5,000,000 red corpuscles. According to these estimates, which have been confirmed by more recent observers, a single grain of human blood contains about 325,000,000 corpuscles. The weight of a single corpuscle may be stated approximately at 1–800,000,000th of a grain, or, according to Harting, at 1–13,114,000th of a milligramme.

The number of red corpuscles is something less in the blood of women than in that of men, and also in arterial than in venous blood, and it even varies in different parts of the same circulation. It also varies in the blood of different animals, even of the same class. Thus, in the rabbit there are about 3,500,000 corpuscles and in the goat about 18,000,000 per cubic millimetre. In general, birds have usually more than mammalia, and cold-blooded far less than warm-blooded animals.

Forms of the Corpuscles.—The red corpuscles of the blood of all vertebrate animals present one or other of two forms, being either *circular* in outline or more or less *oval*. In all *mammalia*, except in embryo, the corpuscles are destitute of a nucleus, while in all *oviparous* animals they contain a nucleus. Hence the former class was designated by Prof. Gulliver, who first pointed out the distinction, the *Apyrenæmatous;* and the latter group, including Birds, Reptiles, and Fishes, the *Pyrenæmatous* Vertebrates.

1. *Non-nucleated Corpuscles.*—In man and all mammalia, except the camel tribe, the red corpuscles are *circular*, flattened, biconcave disks, which have been aptly compared to double concave lenses with rounded edges. As seen under the microscope, the free corpuscles almost invariably present the flat surface to view, Fig. 13. The *thickness* of the corpuscle at its edge is usually between one-third and one-fourth the diameter of the disk.

Fig. 13.



Blood-Corpuscles.—1. Mammalian: *a*, front view; *b*, on edge. 2. Oviparous; front view, showing nucleus.

In the camel tribe, the corpuscles have an *oval* or *elliptical* outline, and the sides are slightly convex. The corpuscles of this tribe, however, conform to those of mammalia in general, in being destitute of a nucleus, and in smallness of size.

In *size* the red corpuscles of the mammalia differ more or less in the different members of the class; and they also vary somewhat in the blood of the same animal. But, as we shall see hereafter, very

close uniformity exists in much the greater proportion of the red corpuscles of the same animal. With only few exceptions, the average diameter of the red corpuscles of mammalian animals varies from 1–3000th to 1–6000th of an inch, or through a range of 1–6000th of an inch. The largest corpuscles of this kind are those of the elephant, having a mean diameter of about 1–2750th of an inch, and the smallest are found in the musk-deer, these measuring about 1–12,325th of an inch, the extreme range being, therefore, about 1–3500th of an inch; that is, the diameter of the largest mammalian blood-corpuscles known is about 1–3500th of an inch greater than that of the smallest known.

In regard to the *structure* of the red corpuscles, histologists have held very different views. By many of the older writers they were regarded as composed of a distinct cell-wall or membrane, filled with a fluid containing the red coloring matter of the blood. But according to more recent observers they consist of a colorless, highly elastic, porous or cavernous mass, or "stroma," albuminous in substance, and the interstices of which are filled by the coloring matter of the corpuscle.

2. *Nucleated Corpuscles.*—In the blood of all birds, reptiles, and fishes the red corpuscles contain a distinct *nucleus*, which is generally oval in form, but sometimes nearly or altogether circular. The nucleus is dark in color, rough in contour, and usually occupies the central portion of the corpuscle, but sometimes it is eccentric. In the blood of birds the nucleus is relatively much more elongated than the corpuscle itself; in reptiles and fishes it has usually the figure of the corpuscle.

The corpuscles in all these classes, except in a small family of fishes (the *Cyclostomata*), are more or less *oval* in form, the ellipticity being greatest in the blood of birds, in which the long diameter of the disk may be, according to Gulliver, twice its short diameter. This difference is somewhat less in the blood of reptiles and least in that of fishes, in which the corpuscles pass by gradations to the circular form.

In *size* the corpuscles of these classes are considerably larger than in the mammalia, the largest being found in the blood of reptiles, especially batrachians. In the blood of the *Amphiuma tridactylum* the corpuscles can be seen by the unaided eye, their length being about 1–350th of an inch.

The flattened sides of the nucleated corpuscles are generally more or less convex, and the thickness of the disks is about one-third their short diameter.

In the *Cyclostomata*, the lowest order of fishes, the corpuscles are circular in form, flattened, and have their sides slightly concave; hence they differ from those of man and the regular mammalia only in the presence of a nucleus and in larger size (1–2100th of an inch). In the *Amphioxus lanceolatus*, a member of this order and the very lowest of vertebrates, there is an entire absence of the red corpuscles, the circulating fluid containing only colorless disks.

Action of Water and Reagents on Red Corpuscles.—The red corpuscles of the blood of all animals are more or less affected by most liquids and certain gases.

1. *Circular Corpuscles.*—*Water*, if added only in very minute quantity to the blood of man or any of the regular mammalia, causes the corpuscles to become thicker and somewhat *diminished* in diameter, the concave sides becoming first flat, then convex, the thickening, according to Frey, beginning in the margins. After a time, or if more water be added, the corpuscles still increase in thickness, become less in diameter, pale in color, and finally entirely decolorized and spherical in form, the diameter being reduced in human blood-corpuscles to about 1–4200th of an inch or less. In this state they are so transparent as to be nearly or altogether invisible to the microscope. The addition of a potassium iodide solution tinged with iodine will render the outlines more distinct, and may render them quite visible after they have disappeared from view.

If the blood be treated at once with a comparatively large quantity of water, the corpuscles are instantly deprived of color, and become globular and nearly or wholly invisible, or they may undergo entire disintegration. Not only is the effect of water thus determined somewhat by the relative quantity employed, but its action differs somewhat, it is said, on the blood of different animals. That the corpuscles, by the action of water, are rendered spherical and *less* in diameter was first observed by Hewson.

If the corpuscles when thus distended be treated with a neutral liquid of greater density, as a solution of common salt, they regain more or less their original forms.

It has long been known that some of the corpuscles in the same

sample of blood resist the action of water very much more than others, the former retaining their color and form long after the latter have entirely disappeared.

In neutral liquids of the same density as the liquor sanguinis, the corpuscles undergo little or no change. In liquids more dense than the serum, they become shrivelled, and crenated or jagged in outline. The caustic alkalies quickly dissolve the corpuscles, ammonia acting more energetically than the fixed alkalies.

2. *Oval Corpuscles.*—The effect of *water* upon corpuscles of *oval* form is much the same as that upon the circular disks. The sides become more convex, the long diameter shortens and the short diameter lengthens, and they become lighter in color. As the action continues, they assume a nearly or altogether spherical form, with a diameter intermediate between the long and short diameters of the original corpuscle, and finally become colorless and exceedingly transparent, or invisible. Thus, under the action of water, the corpuscles of oviparous animals may closely resemble in outline those of mammalia under like conditions; but the presence of the nuclei and their larger size readily distinguish the former from the latter.

Water has little action upon the nuclei, other than to cause them to become more spherical; they may frequently be seen even when the outlines of the corpuscles have become invisible. If the swollen corpuscles be treated with a more dense liquid, they regain their original forms. *Acetic acid* causes the corpuscles to thicken and become transparent, but it does not readily act upon the nuclei.

White Corpuscles.—The *white* or *colorless* corpuscles, known also as *leucocytes*, were first described by Hewson. These have the singular property of amœboid or spontaneous movement, and of absorbing within themselves, when brought in contact, finely-divided coloring matters. Their average proportion in normal human blood is one to about 350 of the red corpuscles; but their number is subject to great variation, depending upon age, sex, and various conditions.

The colorless corpuscles are globular or spheroidal in form, more or less granular, and contain one or more nuclei, which may be either round, oval, or irregular in outline, and sometimes more or less superimposed one upon the other. The colorless corpuscles have a higher refractive power, greater firmness, and are specifically lighter, than the red corpuscles. The nuclei are not generally visible

until the corpuscle is treated with acetic acid or other reagent, which dissolves or renders the granules of the disk more transparent.

In *size* the white corpuscles are pretty uniform throughout the entire Vertebrata, ranging in diameter from about 1–2500th to 1–3000th of an inch, and being, according to Prof. Gulliver, as large in the musk-deer as in ordinary mammals. As is well known, the proportion of the white to the red corpuscles is sometimes very greatly increased in disease (*leucocythæmia*), in which the former may almost equal in number the latter.

Water causes the colorless corpuscles to become smoother in appearance and more transparent, brings to view the nuclei, and finally causes the mass to disintegrate.

Histologists are now generally agreed that the white corpuscles of the blood are identical in general character with the ordinary corpuscles of lymph, chyle, saliva, mucus, and pus.

Identification of Blood.

When in its fresh condition, the physical characters of blood are usually quite sufficient to distinguish it from all other liquids. But as presented for identification in medico-legal investigations, it is generally in the dried state, in the form of stains, more or less minute, which may be recent or old and may have been washed.

Under these circumstances the presence of one or more of the constituents of blood may be established either by their *chemical properties*, by their *optical effects*, or by their *microscopic appearances*, or by these methods combined.

In medico-legal practice, when any account is given of a suspected stain, the primary question usually presents itself under one or other of the following forms: 1st. Is the suspected stain blood? 2d. Is it the blood of an *oviparous* animal? 3d. Is it, or may it be, that of a specific mammal, or may it be human blood? In many instances, however, no explanation of this kind is given or obtained, and the medical jurist has to determine whether the stain is really blood, and, if so, its true character, so far as he can.

Physical Character of Blood-stains.—The color and general appearance of a blood-stain will depend much upon its thickness, age, the nature of the material upon which deposited, and also the condition of the atmosphere to which exposed. The characteristic red color of a fresh stain will after a time change to reddish-brown

or brown. This change may take place even within a few hours. When upon a fabric, dried blood imparts to it more or less stiffness. The *side* of the fabric upon which the stain was received should be noted, and also its exact location on the article upon which found.

For the examination of minute stains, a low power of the microscope, especially with the binocular instrument, with condensed reflected light, may be employed with great advantage. If blood, the stain will present a bright shining appearance and a highly characteristic red color. In this manner coagula may be found even in exceedingly minute stains. Stains upon dark-colored substances may sometimes, it is said, be best detected by artificial light.

Water dissolves the *hæmoglobin*, or red coloring matter, of dried blood, together with the albumen and salts, leaving the fibrin as a nearly colorless film. The red color of the solution, even when containing the coloring matter of only one part of blood in 1000 parts of liquid, may be well marked, especially on looking down the tube in which it is contained; a reddish hue may even be observed in a 1–5000th solution of blood.

A portion of the stained fabric, or the matter scraped from a spot, is treated in a very small test-tube with a little pure water, when, if the stain is recent or comparatively so, the liquid will quickly assume a red color, which at first appears as a red coloration around the stain; but when the stain is older, some hours may be required for its solution, and the liquid may acquire only a brownish hue. The age of a stain cannot always be determined by its solubility in water, since one some months old may dissolve more readily than another only a few weeks old. If the stain has been heated, the coloring matter will generally be insoluble in water; but it may be rendered soluble by the addition of a little alkali. Very old stains usually entirely resist the action of pure water. Any stains removed from a substance for examination should be correspondingly marked.

Any solution thus obtained may now be examined by the chemical tests, or by means of the spectroscope, for blood.

II. Chemical Tests for Blood.

1. *Heat.*—If an aqueous solution of blood be heated to near the boiling point, its red color is quickly discharged, with the formation of a dirty-brownish precipitate or turbidity, due to the coagulation

of the albumen; the upper portion of the liquid usually presents a faint yellow hue. A 1–1000th solution of blood will yield only a marked turbidity of a light color.

If a drop of sodium hydrate solution be now added, the precipitate or turbidity immediately disappears, and the liquid acquires a more or less red color by reflected and a greenish hue by transmitted light, being dichroic. The precipitate may be reproduced by adding a drop of nitric acid. If a few drops of the acid be allowed to flow down the side of the tube and quietly subside to the bottom, a white zone will appear at the surface of contact of the two liquids, even if only 1–1000th of blood be present.

The immediate discharge of the red color of solutions of blood, with the formation of a coagulum, when heated, distinguishes it from the red extracts of roots, fruits, flowers, and dyes, which are unchanged by heat.

2. *Ammonia.*—When diluted and added in limited quantity, ammonia has little or no action upon the red color of solutions of blood; if added in large quantity, the solution will assume a brownish hue. A minute quantity of ammonia really heightens the color of a blood solution. Under the action of this reagent the red color of vegetable extracts, cochineal, and certain mineral substances is either changed to green, violet, crimson, or blue, or entirely discharged, depending upon the nature of the coloring matter.

3. *Guaiacum Test.*—On treating a solution of the coloring matter of blood with an alcoholic tincture of *guaiacum* and an ethereal solution of *hydrogen peroxide*, a deep blue coloration is produced, due to the oxidation of the guaiacum resin. The alcoholic solution should be freshly prepared from inner portions of the resin. The ethereal solution of peroxide of hydrogen, known in the shops as *ozonic ether*, may be prepared by suspending some pure barium dioxide in water, adding an equivalent quantity of dilute sulphuric acid, and extracting the liberated hydrogen peroxide by ether. A portion of the ether extract, if fit for use, will strike a beautiful blue or violet coloration on the addition of a fragment of chromic acid.

In applying this test, a drop of the blood solution, placed over a white surface or in a porcelain dish, is first treated with a drop of the guaiacum tincture, and then a drop of the ether reagent added, when, even if only a trace of the coloring matter of blood be present, a blue color will immediately or very quickly appear. A drop of a

1–1000th solution of blood will thus immediately yield a decided blue coloration; and a 1–5000th solution a quite distinct reaction.

The test may be applied directly to the stain, if on a white fabric, by moistening it with a drop of water, and then adding the guaiacum and ethereal solutions. Even the minutest shred of a blood-stained fabric may show this coloration. When the stain is on colored material, it may be, as advised by Dr. Taylor, thoroughly soaked with a drop of water, and the liquid absorbed by slips of white bibulous paper; these, while still moist or after they have dried, are submitted to the action of the reagents.

This test will react even with very old stains, provided they are first well moistened with water; and even when the stains have been washed, evidence of their nature may be obtained.

In one of our experiments, a piece of muslin 1–10th of an inch square, containing a moderate blood-stain of ten years' standing, was macerated with a few drops of water for ten hours; the liquid, which had acquired only a faint reddish hue, was then decanted and evaporated spontaneously, when it left a smooth, ring-like deposit of a faintly reddish-yellow color. This, under the action of the test, immediately assumed a deep blue color. So, also, a minute portion of a single thread of the soaked material immediately acquired a deep blue color on the application of the reagents.

For the extraction of the coloring matter of very old blood-stains, M. Blondlot strongly advises (*Annales d'Hygiène*, 1868, i. 130) the use of *ammoniated alcohol* (1 : 20). This we have found a very good mixture for the purpose. A little potassium hydrate (free from nitrite) may also be used for the extraction, the liquid being neutralized with acetic acid before adding the guaiacum tincture. D. Vitali has observed that guaiacum, when precipitated from its alcoholic solution by water in the presence of hæmoglobin, carries down with it the whole of the latter, even, he states, when forming only 1–100,000,000th of the liquid. The precipitate is then collected and tested by the ether solution. (*Jour. Chem. Soc. Abst.*, 1880, 926.) On collecting the precipitate, however, according to our experience, it sometimes acquires a faint blue color even in the absence of blood and before the ether reagent is added, due to slow oxidation.

For the recovery of the blood coloring matter when under great dilution in water, the urine, and other liquids, it may be precipi-

tated, as advised by Schwarz, by zinc acetate. The solution is treated with a little of the salt, and the mixture allowed to stand several hours, or until the precipitate has completely subsided; the latter is then collected on a filter, washed, and tested by the guaiacum and ether reagents. In this manner we have obtained very satisfactory evidence of the presence of blood when forming only 1–50,000th of the solution.

Fallacies.—As the bluing of the guaiacum resin in this test is simply due to oxidation, a like result is produced by various other substances, organic and mineral, especially certain salts of iron, even in very minute quantity. But all these substances, according to Dr. Taylor, who has critically examined this test (*Guy's Hosp. Reports*, 1868, 431), effect the bluing *without* the aid of the hydrogen solution; whereas blood does not; moreover, they have not the color of blood. According to this author, there is no red coloring matter known, other than that of blood, that will yield these results under the action of the test. If the reagent solutions be applied in a state of mixture, as is sometimes advised, the results are open to serious objections. In the examination of a suspected stain, the result of the guaiacum solution alone should first be determined; and after the addition of the ether reagent the blue coloration should appear very promptly, otherwise the result would be very doubtful.

4. *Hæmin Crystals.*—When heated with acetic acid and a little common salt, the hæmoglobin of the blood undergoes decomposition, with the formation, as one of its products, of *hæmatin*, which, uniting with hydrochloric acid produced from the sodium chloride, forms *hæmatin hydrochloride*, or *hæmin*. This compound readily crystallizes, forming what are known as *Teichmann's* crystals, he having first described them, in 1853; its composition, according to Hoppe-Seyler, is $C_{68}H_{70}N_8Fe_2O_{10},2HCl$. For its preparation, the blood should be in the dried state, and only the most concentrated glacial acetic acid employed.

When the blood is in solution, a drop of the liquid is evaporated to dryness on a thin glass slide or in a watch-glass, the residue scraped together and pulverized, a trace of finely-powdered salt added, and then a drop or two of the acid. The heat of a very small flame of a spirit-lamp is now applied to the mixture, first around and slightly beyond the edges of the dispersed liquid, until it has collected on the centre of the slide in the form of a globule. This is then heated

until bubbles of gas appear and the liquid acquires a reddish-brown color, when the heat is gradually withdrawn until only a minute portion of liquid remains, this being allowed to evaporate by the heat of the slide.

The residue thus obtained usually consists of brownish-red lines or stains, more or less curved or circular in form. Under the microscope the hæmin will appear as minute crystals, of a yellowish, reddish, or brown color, more or less transparent, and frequently arranged in the form of stellate groups, Plate XV., fig. 5. When from only a minute quantity of blood, the crystals are single, and usually range in size from 1–1200th to 1–1800th of an inch in length, and from 1–6000th to 1–12000th of an inch in width.

Under this test, 1–100th of a grain of blood will yield a residue in which the crystals may readily be recognized under a power of 75 diameters. From 1–500th of a grain the crystals are usually so minute as to require a high power for their identification, Plate XV., fig. 6. With care, crystals may be obtained from even the 1–1000th of a grain of blood.

Sometimes the hæmin, even under a high power, is in the form of opaque, irregular granules. When this is the case, the residue is again treated with a trace of salt and heated with acetic acid. Unless the blood-stain be very old or had been washed, the addition of the salt is not essential, as the quantity normally present in blood is sufficient for the purpose. It is always best, however, to add a minute quantity of salt, as its crystals interfere but little with the recognition of those of hæmin, and they may readily be removed by a drop of water.

Hæmin crystals are insoluble in water, alcohol, and acetic and hydrochloric acids, sparingly soluble in ammonia, but freely so in the fixed alkalies. Under the action of the guaiacum test, they immediately assume a deep blue color. The crystals may be mounted in Canada balsam and thus preserved indefinitely.

When the stains are very old or have been washed, and also when they are recent, a small portion of the stained fabric or of the dried clot may be heated in a very small test-tube with a few drops of the acetic acid and a little salt to about the boiling temperature, until the liquid acquires a reddish or brown color. The liquid is then transferred by a capillary pipette to a watch-glass and evaporated as above directed. In this manner a very satisfactory crystalline

residue was obtained from 1–10th of an inch square of a fabric containing a blood-stain ten years old.

So long as any of the coloring matter or hæmatin remains undecomposed, crystals may be obtained by this test. But it must be borne in mind, as pointed out by Struve, that a blood-stain may have undergone such change as no longer to respond to this test, its color being due to the products of decomposition. Hence a failure to obtain crystals should not be regarded as proof of the absence of blood. Moreover, it is sometimes quite difficult to obtain crystals from minute quantities of blood, even when recent. And, again, the presence of certain substances, especially free acids, except acetic acid, may interfere with their formation.

Various methods have been advised for the precipitation of the coloring matter of the blood when under great dilution for the application of this test. That by acetate of zinc has already been mentioned when considering the guaiacum test. Another is to treat the solution with a little ammonia, then tannic acid, and finally excess of acetic acid, and allow the mixture to stand twelve or twenty-four hours. The dark brownish precipitate is collected, washed, and subjected to the action of the test, a portion being examined by the guaiacum method. Satisfactory results may be obtained by this, as also by the zinc method, from solutions containing only 1–50,000th of blood.

Fallacies.—The forms and appearances of hæmin crystals are so peculiar and striking that they could not be confounded, at least by any one familiar with their characters, with any other substance. Their production is characteristic of blood, there being no other substance known from which they can be obtained.

It has been asserted that the crystals from the blood of different animals differ somewhat in appearance; but this is an error, since they are essentially the same in form and character as produced from the blood of all vertebrate animals.

Of the various other *chemical methods* that have been proposed for the detection of blood there need only be mentioned that of M. Sonnenschein (1873). This consists in treating a solution of the stain with a solution of sodium molybdate or tungstate strongly acidulated with acetic or phosphoric acid, whereby a precipitate is produced which under a gentle heat collects into a pulverulent, brownish mass. This,

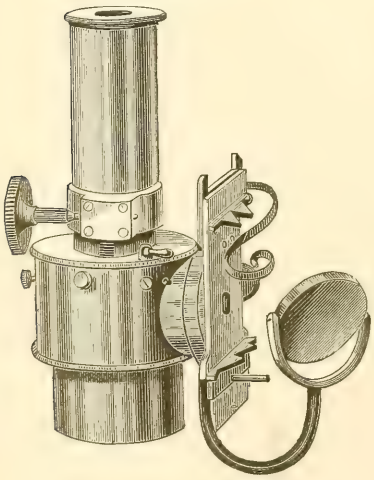
when collected and gently heated with a few drops of aqua ammoniæ, dissolves to a solution which appears of a dark red color by reflected, and greenish by transmitted, light. This dichroism will still appear when obtained from a blood solution so dilute as to have only a faint red color. The precipitate is reproduced on addition of excess of acetic acid, and may then be examined by the guaiacum test.

III.—Optical Properties of Blood.

History.—When light that has passed through a solution of blood is received upon a prism, the spectrum produced presents characteristic black bands, the corresponding portions of the light having been absorbed by the coloring matter of the blood. This fact was first observed by Hoppe-Seyler, in 1862, and he proposed it as a means of detecting the presence of blood in medico-legal investigations.

A few years later, 1864, Prof. Stokes found that two distinct spectra might be obtained from the blood, depending upon the state of oxidation of its coloring matter, the one corresponding to arterial blood and the other to deoxidized or venous blood. Further researches have shown that under the action of chemical reagents a number of characteristic spectra may thus be obtained from hæmoglobin, and its products and compounds.

Fig. 14.



Sorby's spectroscope eye-piece.

Application.—For the application of this method in connection with the microscope, the instrument known as the Sorby-Browning spectroscope eye-piece, or micro-spectroscope, is admirably adapted, Fig. 14. This instrument permits two spectra to be examined at the same time, and thus the spectrum of the suspected substance may be compared side by side with that of a known sample of blood. Any microscope, provided the eye-piece fits, will answer this purpose; but it is somewhat more convenient

to employ a binocular instrument. Only low powers, such as the one and a half or two-thirds inch, are required for the examination. It is well to cut off all extraneous light from the front of the objective by placing over it a capped tube having a small perforation in the centre of the cap.

The solution to be examined may be placed, as advised by Mr. Sorby, in small cells about half an inch deep, made from barometer tubing, and cemented to a glass plate. These cells permit the examination of a long column with only a small amount of fluid, and are convenient for the addition of reagents. But the examination may be made with a small drop of the solution placed simply on a glass slide. Either ordinary or artificial light may be employed: the latter is usually to be preferred.

The focus of the microscope having been adjusted to the surface of the blood solution, and the slit of the spectroscope so narrowed as to allow only sufficient light to pass, the appearances presented will depend somewhat on the age of the blood, the strength of the solution, and also, in part, the length of the column of fluid examined.

1. *Oxy-Hæmoglobin.*—When the blood is fresh and the solution not too strong, more or less of the blue end of the spectrum is absorbed, and two characteristic bands appear in the green portion of the spectrum. Of these bands, the one towards the red end of the spectrum nearly or altogether touches Fraunhofer's line D, is darker in appearance, sharper in outline, and narrower than the other, which is placed near the line E, Chromo-lithograph, Spectrum 2. In stronger solutions these bands unite, and may occupy the entire space between D and E.

In a deep cell, such as above described, a solution containing 1–500th of its weight of blood gives the spectrum in great perfection; in a 1–1000th solution the bands are still well marked, though somewhat narrowed. Under much dilution, the band next Fraunhofer's line E diminishes in intensity more rapidly than its fellow. The delicacy of this test is such, in fact, that with proper manipulation, as first announced by Mr. Sorby, a faint spectrum may be obtained from even a single blood-corpuscle.

These results are wholly due to the oxy-hæmoglobin of the blood, of which it forms only about one-eighth by weight. The differences observed in the spectra of solutions of oxy-hæmoglobin

of varying degrees of dilution have been described and figured by W. Preyer. (*Die Blutkrystalle*, Jena, 1871.)

2. *Hæmoglobin.*—If a solution of fresh blood be treated with a little ammonia, the two bands become somewhat narrowed and sharper in outline. On now adding a little citric or tartaric acid, avoiding excess, and then stirring in the solution a minute crystal of ferrous sulphate, preventing free access of air, the liquid acquires a purple color, and exhibits under the spectroscope a single broad band, extending over and beyond what was the space between the two former bands, Spectrum 3.

This is the spectrum of *hæmoglobin*, known also as *reduced hæmoglobin*, and may be seen in blood-stains or solutions that have become more or less brown. This reduction may also be effected by ammonium sulphide, without the other reagents. On agitating the reduced mixture with air, the two bands of oxy-hæmoglobin reappear.

If in this experiment the citric or tartaric acid be added first, and then the ammonia and iron salt, the mixture assumes a brown color and presents the spectrum of *reduced hæmatin*.

3. *Methæmoglobin.*—In blood that has been exposed to the air for some time and become more or less brown, there is gradually formed a substance named by Hoppe-Seyler *methæmoglobin*. The exact nature of this substance is not yet fully understood. According to Hoppe-Seyler, it is an oxide of hæmoglobin containing less oxygen, and this more firmly combined, than is present in oxy-hæmoglobin. (*Physiol. Chem.*, 1881, 391.) This compound may be produced at once by treating a solution of blood with potassium permanganate solution.

The spectrum of *methæmoglobin* presents a deep band in the red, and usually two bands more or less faint in the green, Spectrum 4. In the conversion into this substance, the band in the red, at first only very feeble, gradually increases in intensity, whilst the bands in the green gradually become more feeble and are finally lost. Mr. Sorby found that while it usually required some weeks to effect this change in a pure country atmosphere, it might take place within a few hours in the impure air of a city. We have seen the change only moderately marked in a stain three weeks old.

If a little ammonium sulphide be added to the methæmoglobin solution, the band in the red disappears and the broad band of hæmoglobin appears in the green. This may now be oxidized, by

exposure to the air, to oxy-hæmoglobin. Methæmoglobin has recently been obtained in the crystalline state by Hüfner and Otto. (*Zeits. f. Phys. Chem.*, vii. 1883, 65.)

4. *Hæmatin.*—When blood is exposed to the action of the air for long periods, the hæmoglobin undergoes complete decomposition, giving rise, with other products, to *hæmatin*, which is more stable in its nature than hæmoglobin, and may resist decomposition for many years. A stain in which this change has taken place is no longer soluble in water, but may be dissolved by diluted acids.

This conversion is effected immediately on treating fresh blood with an acid. Hence, if a solution of blood, either fresh or old, be treated with a little acetic or citric acid, the spectrum of *acid hæmatin* will appear, in which there is an absorption band in the red and another in the green, Spectrum 5. Sometimes, according to the strength of the solution, the band in the green is absent, whilst at other times two faint bands may be seen in the green. It need hardly be stated that when hæmatin has once been formed, it is no longer possible to obtain the spectra of hæmoglobin and its oxides.

5. *Alkaline Hæmatin.*—If to the solution of acid hæmatin slight excess of ammonia be added, the spectrum of *alkaline hæmatin*, having a single broad band in the red, will manifest itself, Spectrum 6. With stronger solutions, according to Preyer, the band extends beyond the line D.

6. *Reduced Hæmatin.*—On adding a little ferrous sulphate to the last-mentioned solution, it will exhibit the spectrum of *reduced hæmatin*, Spectrum 7, as figured by Preyer. This spectrum closely resembles that of a somewhat dilute solution of oxy-hæmoglobin, only that the two bands are slightly moved towards the blue end of the spectrum. This substance has been named by Hoppe-Seyler *hæmochromogen.*

The three hæmatin spectra usually exhibit themselves more strongly marked than the spectrum of hæmoglobin under like conditions. These spectra may be obtained from blood-stains after the lapse of many years.

7. *Carbonic oxide Hæmoglobin.*—In fatal asphyxia from carbonic oxide gas, as is well known, the blood acquires a peculiar rose-red color, which it may retain for long periods. In poisoning by this substance, the carbonic oxide unites with the hæmoglobin of the blood to form *carbonic oxide hæmoglobin*, the gas taking the place,

volume for volume, of oxygen in the formation, by the latter, of oxy-hæmoglobin. This compound is not decomposed by the oxygen of the air, and it more strongly resists the action of reducing agents and putrefaction than do the oxides of hæmoglobin.

Accepting Prof. Hüfner's formula for hæmoglobin, the molecular composition of the carbonic oxide compound, according to the researches of my assistant, Dr. J. Marshall, while in Prof. Hüfner's laboratory, is $C_{636}H_{1025}N_{164}FeS_3O_{189},CO$, its molecular weight being 14,157. (*Zeits. für Phys. Chem.*, Jan. 1883, 81.)

The spectrum of carbonic oxide hæmoglobin, shown in Spectrum 8 (after Preyer), is very similar to that of oxyhæmoglobin, only that the two bands are of equal intensity and about equal in width. Its strong resistance to reducing agents readily distinguishes it from the spectrum of oxy-hæmoglobin. Thus, when the solution is treated with a drop or two of ammonium sulphide, the two bands remain unchanged; whereas with oxyhæmoglobin they are immediately replaced by the single band of hæmoglobin. Indeed, Prof. Vogel has proposed this property as a test for the presence of carbonic oxide in the atmosphere, by exposing to the air a single drop of fresh blood, and then adding to the liquid the ammonium salt, when, if the air contains only 0.3 per cent. of the gas, the reduction will be prevented. (*Chem. News*, 1877, i. 184.)

Examination of Suspected Stains.—In the practical application of the spectroscopic method to a suspected stain, the procedure will depend somewhat upon the amount of material at command and the age of the stain. When the stain is fresh, it requires only a small amount of blood to furnish the various spectra above described.

When on a fabric and at least of moderate size, a portion of the stained material is macerated with a little water in a small tube or watch-glass, and any red solution obtained, after subsidence of suspended matters, transferred to a deep cell and examined. If the liquid exhibits the spectrum of oxy-hæmoglobin, a little ammonia may be added, then a minute crystal of citric acid, avoiding excess, and finally a little ferrous sulphate, when, as the latter dissolves, the spectrum of hæmoglobin will appear.

Or, the solution which showed the two bands of oxy-hæmoglobin may be treated with a little citric acid, when the bands will disappear, and the bands of acid hæmatin may or may not appear; on

the subsequent addition of ammonia and then ferrous sulphate, the spectrum of reduced hæmatin will be developed. From dilute solutions this spectrum is more readily obtained than that of reduced hæmoglobin. A blood-stain only 1–10th of an inch square, if readily soluble, will suffice to show these spectra in a very marked degree. If the solution has only a faint red hue, a very narrow and deep cell should be employed. When the stain is on colored material, an equal portion of the unstained fabric should be examined in a similar manner. If the stain is sufficiently thick to permit the separation of solid particles, these should be dissolved in a drop or two of water and examined.

Should the solution first obtained exhibit the spectrum of methæmoglobin, it may be further examined in the manner already indicated. A blood-stain in which this change has taken place may be only partially soluble in water, a portion of the coloring matter having been further changed into hæmatin, which is insoluble in water.

If the stain is old or has been washed, it may be wholly insoluble in pure water. Under these circumstances it is treated with a few drops of water containing a little citric or acetic acid, and digested at the ordinary temperature for several hours, if necessary. Any brownish or yellowish liquid thus obtained is examined for the spectra of hæmatin in its acid, alkaline, and reduced states. In very dilute solutions, as already indicated, the spectrum of reduced hæmatin may sometimes be obtained when there is a failure to obtain that of either acid or alkaline hæmatin. From a stain seventeen years old, in which the coloring matter was wholly changed into hæmatin, Dr. Letheby (*London Hosp. Rep.*, iii. 41) obtained from a portion of the fabric not exceeding one-fourth inch in diameter only faint traces of the spectrum of acid hæmatin, but under the action of ammonia and then of ferrous sulphate he obtained as well-marked spectra as from comparatively recent blood.

If the blood-stain has been heated or washed with hot water, dilute acids will generally fail to act upon it, but it may be dissolved in water containing a little ammonia, especially if the mixture be heated. The solution is then treated with a little citric acid and ferrous sulphate and examined for reduced hæmatin. For this reduction it is somewhat better to substitute for the citric acid the double tartrate of potassium and sodium, and for the iron salt the

double ferrous and ammonium sulphate; or, the ammoniacal solution may be treated at once with ferrous tartrate.

When the stain is only in very minute quantity, it should be carefully examined for any dried clot, which, if found, is placed on a glass slide, moistened with a very minute drop of diluted glycerine (1 : 5), and any solution obtained examined directly by the spectroscope. In this manner we have found, as stated by Dr. J. G. Richardson (*Med. Times*, Nov. 1875, 78), that a clot not exceeding 1–100th of an inch in diameter will yield a very satisfactory spectrum. Dr. Richardson advises to place the minute clot moistened with the glycerine on a thin glass cover, and then invert this over the concaved centre of a slide: it may then, after examination by the spectroscope, be examined under a higher power for the presence of blood-corpuscles, and finally by the guaiacum test. If no clot is found, a shred of the stained fabric may be moistened with diluted glycerine and examined in a similar manner. The solvent action of moderately diluted glycerine upon somewhat old blood-stains is markedly less than that of pure water.

Fallacies.—There are certain other coloring substances that exhibit spectra more or less similar in appearances to those of blood. In his extended examination of various coloring principles, Mr. Sorby found the spectrum of *alkanet root* in alum to bear the closest resemblance in this respect, it having two bands in the green; but the band towards the red is the broader of the two, whereas the reverse is the case in the blood spectrum.

So, also, *cochineal* presents two bands in the green, but these are about equal in intensity and width. Moreover, neither of these substances resists the action of ammonia, nor will they yield the other spectra of blood. It has also been asserted that the coloring matter of the feathers of the banana-eater (*Turacus albocristatus*) of the East Indies exhibits a spectrum very similar, both in position and appearance of the bands, to that of fresh blood; but it is said to be unaffected by sodium sulphide, which quickly changes the character of the blood spectrum.

Prof. Reichardt has asserted (*Arch. d. Pharm.*, 1875) that the spectrum of *purpurin sulphuric acid* might be confounded with that of alkaline hæmatin. According to Dr. Ch. Gänge, of Jena, however, this substance yields its spectrum only from *warm* solutions, and the band lies between D and E, whilst that from blood is

between D and C; moreover, although the spectrum of potassium purpurin sulphate bears great similarity to that of hæmoglobin, yet it remains unchanged on exposure to the air, whereas hæmoglobin is oxidized to oxy-hæmoglobin.

Hence these fallacious substances differ from blood in most instances in the position and character of the spectral bands, and in *all* cases in the effect of reagents upon their solutions. At present there is no substance known that in all these respects is similar to the coloring matter of blood.

The methods thus far considered simply serve to answer the question whether or not a suspected stain or substance is blood, the results, when positive, being common to the blood of man and all animals having red blood. Any further determination as to whether it is, or may be, the blood of man, or the kind of animal from which it was derived, can, so far as at present known, be made only by means of the microscope in determining the character of the *blood-corpuscles*. It is true that many years since (1829) M. Barruel proposed to treat the blood with concentrated *sulphuric acid*, when, as he claimed, a peculiar *odor* would be evolved resembling that of the cutaneous exhalation of man or the animal from which the blood was derived. But numerous observers have long since shown that no reliance whatever could be placed in this method, even when applied to fresh blood and in comparatively large quantity. So, more recently, Adolph Neumann proposed to evaporate the blood solution to dryness at about 15.5° C. (60° F.), when the residue would, under the microscope, present appearances or "pictures," whereby the blood of man could be distinguished from that of animals and these from one another. Numerous colored illustrations of the appearances thus presented by different bloods are given by this observer. (*Die Erkennung des Blutes bei gerichtlichen Untersuchungen*, Leipsic, 1869.) On examining this method, however, we find no constancy in the appearances of the same blood, and even different portions of the same residue may exhibit widely different appearances.

IV. Microscopic Determination and Discrimination of Blood.

Oviparous Blood.—In judicial investigations, as already stated, it is sometimes very important to determine, at least, whether the

blood is that of an oviparous animal or that of a mammal. We have already seen that the blood-corpuscles of all oviparous animals, including birds, reptiles, and fishes, are oval in form, except in a small family of the last-named class, in which they are circular; whereas in the blood of all mammals, except the camel tribe, they are circular in outline. Moreover, in the former group of animals, without exception, the corpuscles have each a nucleus, whilst in the latter and in man they are destitute of a nucleus. Hence this question is one of ready solution in fresh blood; but when the blood is in the form of dried stains the distinction may be difficult, or even impossible, especially if the stains are old.

When in the *dried* state, a small clot, or a thread of the stained fabric, is treated on a glass slide with a drop of diluted glycerine (1:10), then covered with a thin glass, and examined under a power of about 400 diameters. Sooner or later, according to the age of the blood, unless very old, the mass will disintegrate and the corpuscles may be seen of their distinctive characters. For this purpose it is generally more satisfactory to employ a clot, even if only very minute, than a stained fibre.

If the clot is so old and dry as not to disintegrate under the action of the diluted glycerine, the moistened mass is gently crushed and then examined. It is sometimes better, in order to prevent the distribution of the liquid, to place the crushed clot on the thin glass cover, and then, after addition of the glycerine, invert this over a shallow glass cell attached to a glass slide.

On examining a crushed mass of this kind under the microscope, the nuclei, if oviparous blood, and the outlines of the corpuscles of normal form, may sometimes be distinctly seen in the thinner portions and margins of the particles before any disintegration of the mass itself has taken place. We have thus seen the nuclei and outlines most distinctly marked in thin portions of oviparous bloods that had been loosely preserved in paper for over ten years. At times only the nuclei are to be seen, the outlines of the corpuscles themselves being wholly invisible. After a time the corpuscles become more or less detached from the entangled mass, and then their nature may be readily determined.

It must be remembered that if the blood be treated with excess of a liquid specifically lighter than itself, the oval corpuscles may become nearly or altogether spherical in outline; but under these

circumstances the nuclei will still be seen, they being generally much more strongly marked than the outlines of the corpuscles themselves. When the outlines are not well marked or are invisible, they may often be rendered distinct by the addition of a little iodine solution. Carmine and aniline may also be employed for this purpose. Much may often be done in rendering the outlines visible by simply changing the light from the mirror of the microscope.

The following method for this differentiation, advised by Dr. R. M. Bertolet (*Amer. Jour. Med. Sci.*, Jan. 1872, 128), may sometimes be used with great advantage. The dried blood is treated with a small drop of pure *glycerine* slightly acidulated with acetic acid, whereby the nuclei, when present, are rendered more distinct. On now adding a little fresh tincture of guaiacum, and then a drop of "ozonic ether," the nuclei will appear sharply defined and of a dark blue color, while the surrounding portions of the corpuscles will have a delicate violet hue or may remain uncolored. With recent blood and that of moderate age this method yields well-marked results; but with older stains the guaiacum reagents produce little or no effect, since the coloring matter is then unacted upon by pure glycerine.

Mammalian Blood.—When the foregoing examination has shown, or it is admitted, that the blood is that of a mammal, the question may then arise, In how far can the blood of man and the blood of other mammals be distinguished from each other?

Our ability to answer this question will obviously depend upon, (1) how far the red corpuscles of the different mammals differ from one another in average size; and (2) our ability to appreciate or measure such differences. Reversing the order of these propositions, we may consider,—

1. Limit of Determining Differences.

a. By the unaided Eye.—With an ordinary rule divided into 1–100ths of an inch the unaided eye will measure the distance between two points, or the centres of two fine lines, with considerable accuracy to within one-half division, and in some cases even less,—that is, to within 1–200th of an inch, or less. By transmitted light, fine lines ruled on glass, with their centres 1–200th of an inch apart, are, with the interspaces, readily distinguished by the naked eye.

Very minute differences in the *size* of objects may thus be detected.

Thus, if two discoidal diatoms (*arachnoidiscus*) measuring respectively 1–139th and 1–166th of an inch in diameter be placed side by side on a glass slide, they are readily discriminated in size by transmitted light, although their diameters differ by only 1–854th of an inch. It is true that the difference of the areas in this instance aids the eye in the distinction, this difference being, however, only 1–82,317th of a square inch.

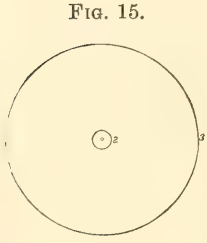
In like manner, as we have found by experiment, many persons can readily distinguish, by the unaided eye, the long from the short diameter of a single oval blood-corpuscle of the *Proteus*, measuring 1–450th by 1–850th of an inch, the difference of the diameters being 1–956th of an inch.

b. By the Microscope.—Our ability thus to discriminate minute differences will obviously be increased in proportion as the size of the object is *apparently* increased. As is well known, it is not the object itself that is seen in the eye-piece of a compound microscope, but the *image* of the object placed upon the stage.

Thus, under an amplification of *ten* diameters, the 1–1000th of an inch of an object becomes apparently 1–100th of an inch; and under a power of one hundred, the diameter of an object is increased one-hundredfold, the 1–10,000th of an inch now being represented by 1–100th of an inch. So, in like manner, under one thousand diameters, the 1–100th of an inch of the *image* corresponds to only 1–100,000th of an inch of the object, and now the latter can be measured to within the 1–100,000th of an inch with the same degree of accuracy that an ordinary object can be measured to 1–100th of an inch by the unaided eye.

The effect of amplification is strikingly shown in Fig. 15, in which the inner circle or disk represents the apparent size of an object 1–1000th of an inch in diameter under a power of 10 diameters; the second, the same under a power of 100; and the outer, the original when amplified 1000 times.

Fig. 15.



If three blood-corpuscles, measuring respectively 1–3000th, 1–3500th, and 1–4000th of an inch in diameter, be examined under a power of 400 diameters, they will appear, in round numbers, 13–100ths, 11–100ths, and 10–100ths of an inch in diameter; under 1000 diameters, 33–100ths, 28–100ths, and 25–100ths of an

inch; and under a power of 2500, they will measure 83–100ths, 71–100ths, and 62–100ths of an inch respectively. Under the last-named power, there would be an *apparent* difference of 1–100th of an inch in the diameters of two corpuscles measuring respectively 1–3200th and 1–3240th of an inch in diameter.

In the amplification of blood-corpuscles, however, there is a limit beyond which any increase of apparent size is attended with more or less loss of sharpness of outline, which is essential for exact measurement. Exactly where this limit lies will depend much on the excellency of the optical parts of the instrument employed.

Measurement by the Microscope.

Stage Micrometer.—Among the appliances necessary for micrometric measurement is a *stage micrometer* of known value. This usually consists, according to English measurement, of a series of fine lines ruled upon glass at a distance from each other of 1–100th of an inch, one of the divisions being subdivided into tenths, or thousandths of an inch. Other fractions of an inch are sometimes added to the scale.

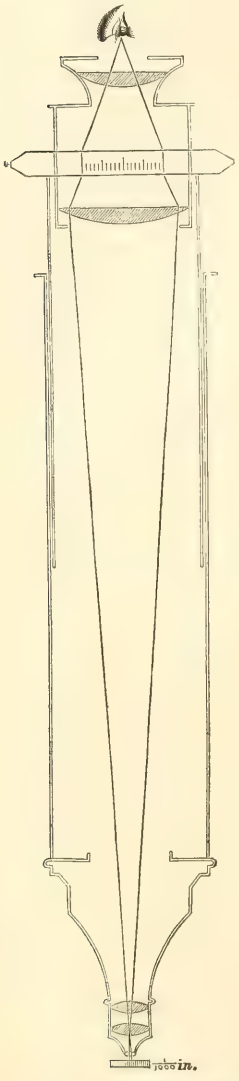
As these subdivisions of 1–1000th inch, as found in scales, are by no means always exactly equal, the scale before being used should be carefully examined in this respect, under a high power. If it is found that the spaces are unequal in value, it should then be determined whether, at least, any one of the subdivisions represents exactly the one-tenth of the 1–100th inch division, and this, if found, should be employed as the standard. We have seen scales in which the discrepancy between certain spaces amounted to 1–35th of a subdivision (1–35,000th of an inch).

Eye-piece Micrometer.—Employing the stage micrometer as the standard, measurements may be made by means either of a *cobweb micrometer*, the *eye-piece micrometer*, or the *camera lucida*. Of these methods, and others that might be mentioned, only that by means of Jackson's eye-piece micrometer will be considered.

This consists of short lines ruled on a slip of glass, every fifth line being longer, and the tenth still longer than the others, to facilitate counting. The slip is placed in a brass frame, and so arranged that its position may be somewhat changed by a fine screw at one end of the frame. Thus mounted, it is placed through slits in the eye-piece just above the diaphragm. If its lines, when thus

placed, are not sharply defined, the eye-lens of the eye-piece is unscrewed until perfect definition is obtained.

Fig. 16.*



1–20,000th inch micrometry.

The value of the divisions of the eye-piece micrometer will of course, other conditions being equal, vary with the power of the objective employed. To determine their value for any given objective or combination, it is only necessary to place one of the divisions of the stage micrometer in focus on the stage of the instrument, and then observe how many divisions of the eye-piece micrometer are covered by it, bringing the lines of the two scales into coincidence by means of the screw in the end of the eye-piece micrometer.

For example, if the 1–1000th of an inch of the stage scale when examined under, say a 1–12th inch objective, should cover eighteen divisions of the eye-piece micrometer, then obviously each division of the latter would have a value of 1–18,000th of an inch. If now the *draw-tube* of the instrument be withdrawn more or less, the 1–1000th of an inch may be made to cover *exactly* twenty spaces of the eye-piece scale, when each division of the latter will represent just 1–20,000th of an inch, Fig. 16.

But it must be borne in mind that this will be true only so long as the then present conditions are observed. Hence we should now accurately note (1) the position of the *draw-tube*, which should be graduated; (2) the position of the *eye-lens*, in case it has been unscrewed to obtain definition of the lines of the scale; and (3) the position of the *screw-collar* of the objective for adjustment of thick-

* Although this drawing is not strictly accurate, and the scales are necessarily greatly out of proportion, yet it will serve to illustrate the general principle of micrometry.

ness of cover, the stage-scale being covered by glass of the thickness most likely to be used afterward in the measurement of objects. So, also, the position of the *fine-adjustment* of the microscope should be noted, and this should be practically the same in future measurements.

Under objectives of still higher power the value of each division of the eye-piece scale may be reduced to 1–40,000th or 1–50,000th of an inch, or even less. The last-named value would require an amplification of about three thousand diameters. The amplification of any given objective will, of course, depend much upon the stand and the eye-piece with which it is employed.

Application.—Having established the value of the divisions of the eye-piece scale for a given combination, the object to be measured is brought into focus and then the number of divisions of the scale it covers read off, just as in measuring an object with an ordinary rule. Thus, if under a micrometry of 1–20,000th of an inch a blood-corpuscle covered just five divisions of the scale, its diameter would be $\frac{5}{20,000}$, or $\frac{1}{4000}$, of an inch; whereas if it covered eight divisions its diameter would be $\frac{8}{20,000}$, or $\frac{1}{2500}$, of an inch. In these readings one of the long lines of the micrometer scale should be made, by means of the fine screw at the end of the scale, just *coincident* with the margin of the corpuscle, and the number of divisions read from this line.

Since the micrometer scale is amplified by the power of the eye-lens of the eye-piece, each division may again be divided by the eye into fractional parts. After many experiments on this point, we find that a practised eye, especially if accustomed to reading minute scales into tenths, will read these subdivisions with very considerable uniformity to the *tenths* of a division. Hence, if the whole division had a value of 1–20,000th of an inch, one-tenth of the division would represent only 1–200,000th of an inch.

In confirmation of the close coincidents that may be obtained in readings of this kind may be cited the results of three independent observers in measuring the 1–1000th inch divisions of a stage scale, the question being, If the ninth division of the scale measures twenty divisions of the eye-piece micrometer, what is the relative value, under the same power, of the other divisions? The results were as follows:

Observers.	Divisions of Scale.									
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
W.	19.7	20+	19.6	20	20	20—	19.8	19.6	20	19.6
M.	19.7	20	19.6	20	20—	20	19.8	19.7	20	19.5
H.	19.7	20.1	19.6	20	19.9	19.9	19.8	19.7	20	19.6

As will be observed, the readings, which were made upon different instruments, did not differ at most to exceed the 1–200,000th of an inch.

In support of this uniformity might also be cited two independent series of measurements of *twenty* designated blood-corpuscles varying in size, under a micrometry of 1–20,000th of an inch, from 6.6 to 5.0 divisions (1–3030th to 1–4000th of an inch), in which the results for each corpuscle were identical except in four instances, and in each of these the discrepancy was only 0.1 division.

In order to ascertain to what extent the results might vary under different powers within a certain range, and by different methods of measurement, seven human blood-corpuscles, gradually varying in size from about the largest to the smallest found in this blood, were selected. These were measured under powers ranging from 1150 to about 3500 diameters, with widely different values of the micrometer; and also by the cobweb micrometer, and by the camera. The averages of the seven corpuscles under these various measurements ranged from 1–3224th to (by the camera) 1–3275th of an inch, the mean of the averages being 1–3236th of an inch. A subsequent and independent measurement of the same corpuscles by Dr. J. G. Richardson with a cobweb micrometer gave an average of 1–3266th of an inch, the difference between this and the former final average being something less than 1–350,000th of an inch.

2. Average Size of Mammalian Corpuscles.

Repeated experiments of our own have shown, as stated by several observers, that, as a general result, the blood-corpuscles on drying in very thin layers on a glass slide undergo no appreciable change in diameter. When they have once attached themselves by their flattened sides to the glass, they remain unchanged for at least many years.

Distribution for Measurement.—It requires some little experience

properly to distribute the corpuscles for measurement; and various methods have been advised for this purpose. A very good method is to moisten a small conical roll of soft paper having a free end with the blood, and then draw this over the slide. The best method yet proposed, however, according to our experience, is that of Prof. Christopher Johnston, of Baltimore. This consists in applying a little of the blood to the well-ground end of a slide, and then drawing the latter, slightly inclined, over the face of another slide or over a thin glass cover. In this way the corpuscles may be very evenly distributed, with rarely any change of their form and very few being in actual contact. If the preparation is for permanent mounting, the blood should be spread upon a thin glass cover.

If on examining the slide with the microscope any notable number of the corpuscles should be of irregular form or have crenated edges, the slide should be rejected for standard measurement. Sometimes these irregularities will be observed only in portions of the deposit. But even when no such change in form is apparent, the corpuscles sometimes *diminish* to a marked extent in diameter before becoming dry, especially in a moist atmosphere. In no case should the measurement of a corpuscle of irregular form be accepted: so soon as it has changed in this respect it is, of course, no longer normal.

Uniformity in Size.—Some years since, Prof. Schmidt announced that at least from 95 to 98 per cent. of the corpuscles of the same animal were equal in size; and this statement is frequently repeated at the present day. To what extent they *appear* of the same size, however, will depend much upon the power under which they are examined. On the other hand, it is sometimes loosely asserted that the corpuscles of man vary from 1–2000th to 1–4000th of an inch in diameter, implying, apparently at least, that there is but little uniformity in this respect.

In regard to the extent of this uniformity in the corpuscles of human blood, the following series of observations may be cited.

(1) On a well-spread slide of human blood five hundred corpuscles were measured in the order presented by a mechanical stage, under a power of 2300 diameters and a micrometry of 1–40,000th of an inch, every corpuscle of normal form being included.

The averages of this series by *fifties* and then by *hundreds*, in the order measured, ranged as follows:

Averages.	Maximum.	Minimum.	Difference.
By fifties . .	1–3213th inch.	1–3292d inch.	1–133,880th inch.
" hundreds .	1–3222d "	1–3274th "	1–202,862d "

Of the five hundred corpuscles:

385, or 77.0 per cent., measured from 1–3077th to 1–3389th of an inch.
42, " 8.4 " " " 1–3389th " 1–3636th " "
20, " 4.0 " " " 1–3636th " 1–4000th " "
49, " 9.8 " " " 1–3077th " 1–2898th " "
4, " 0.8 " " " 1–2898th " 1–2817th " "

The mean average of the five hundred corpuscles was 1–3255th of an inch. Only *one* corpuscle in the series measured over 1–2857th of an inch, and only *two* less than 1–3846th of an inch, in diameter. Two hundred and seventy of the corpuscles, or 54 per cent., fell in size within a range of 1–50,000th of an inch.

(2) A second like series, from a different sample of human blood, examined under a power of 1150 diameters and a micrometry of 1–20,000th of an inch, gave the following results:

Averages.	Maximum.	Minimum.	Difference.
By fifties . .	1–3215th inch.	1–3275th inch.	1–175,485th inch.
" hundreds .	1–3228th "	1–3265th "	1–284,850th "

Of these five hundred corpuscles:

361, or 72.2 per cent., ranged from 1–3077th to 1–3389th of an inch.
56, " 11.2 " " " 1–3389th " 1–3636th " "
12, " 2.4 " " " 1–3636th " 1–4000th " "
65, " 13.0 " " " 1–3077th " 1–2898th " "
6, " 1.2 " " " 1–2898th " 1–2817th " "

The mean average of the five hundred corpuscles was 1–3242d of an inch. Only *one* of the corpuscles measured over 1–2857th and only *one* less than 1–3846th of an inch in diameter. Three hundred of the corpuscles, or 60 per cent., fell within a range of 1–50,000th of an inch.

(3) A third sample of similar blood, mounted by Prof. C. Johnston and being thirteen months old, examined under a micrometry of 1–40,000th of an inch, gave as follows:

Averages.	Maximum.	Minimum.	Difference.
By fifties . .	1–3225th inch.	1–3332d inch.	1–100,427th inch.
" hundreds .	1–3236th "	1–3306th "	1–152,831st "

Of the five hundred corpuscles:

406, or 81.2 per cent., ranged from 1–3077th to 1–3389th of an inch.
59, " 11.8 " " " 1–3389th " 1–3636th " "
9, " 1.8 " " " 1–3636th " 1–4000th " "
22, " 4.4 " " " 1–3077th " 1–2898th " "
4, " 0.8 " " " 1–2898th " 1–2758th " "

The mean average of the five hundred corpuscles was 1–3266th of an inch. Again only *one* corpuscle was found over 1–2857th and *one* less than 1–3846th of an inch in diameter. Three hundred and nine of the corpuscles, or 61.8 per cent., fell within a range of 1–50,000th of an inch. Twenty-one of this series, or 4.2 per cent., measured *over* 1–3000th, and nine, or 1.8 per cent., *less* than 1–3636th of an inch.

The mean average of the three foregoing series of measurements is 1–3254th of an inch. Of some twenty other less extended series of measurements of human blood, the mean average was slightly greater than that just stated. So long ago as 1718, Jurin estimated the human corpuscles to be 1–3240th of an inch in diameter. (*Hewson's Works*, note by Gulliver, 216.)

We have repeatedly seen slides of human blood in which no corpuscles were found of less diameter than about 1–3600th of an inch. On the other hand, not unfrequently the corpuscles on different slides of the same blood, or even in certain portions of the same slide, are uniformly smaller in size than usually found in the given blood. This diminution in size in human blood may be so general that very many of the corpuscles measure from 1–3600th to 1–4000th of an inch, or even less, in diameter. This contraction, as already stated, is likely to occur when the blood absorbs moisture before drying. There is strong reason to believe that the corpuscles as they circulate in the healthy blood are even more uniform in size than our measurements would seem to indicate.

Although the blood-disks may thus under certain conditions *diminish* in size, they *never increase*, while under examination, above their normal diameters. Thus, then, whilst the blood of man might,

on account of contraction in diameter of the corpuscles, be confounded with that of an animal having markedly smaller corpuscles, the reverse could never take place. The importance of this fact in certain medico-legal inquiries is quite apparent.

Notwithstanding the possible diminution in the size of the corpuscles, the general coincidence in the measurements of the same kind of blood by different observers and under different conditions is in the main very close. This close coincidence in the case of human blood under different circumstances we have already seen; and equally concordant results might be cited of the measurements of the blood of various animals. For measurements of this kind, when the ordinary eye-piece micrometer is employed, a micrometry of 1–20,000th of an inch is quite as satisfactory as a higher power.

In Disease.—It has long been known that in certain diseases there is more or less change in the *proportion* of the blood-constituents; but according to more recent observers the *corpuscles* themselves may sometimes be altered in size. In *leucocythæmia*, as already stated, the white corpuscles are very greatly increased in number, whilst the colored disks are somewhat diminished in number, but there is little or no change in the mean diameter of the corpuscles.

In *chronic anæmia*, according to Hayem, as cited by Dr. Gamgee (*Physiological Chemistry*, i. 148), the red corpuscles are always *diminished* both in number and in size, their average diameter, it is said, being sometimes so low as 1–3900th of an inch; whilst, according to Dr. Eichhorst, in *progressive pernicious anæmia* the corpuscles are somewhat *increased* in size, their mean diameter being about 1–3000th of an inch.

From an extended series of experiments on different animals, M. Manassein concluded that the corpuscles were *diminished* in size in septicæmic poisoning, by a high temperature, and by carbonic acid gas; whilst they were *enlarged* under the action of oxygen and agents lowering the temperature of the body, as alcohol and quinine, and in acute anæmia. (*Centralblatt f. Med. Wiss.*, 1871, 689.)

In the following table of the average size of the normal blood-corpuscles of different animals, our own measurements were made in some instances while the blood was still fluid, but generally only after the corpuscles had dried in very thin layers. The average in

each case, expressed in vulgar fractions of an English inch, is the mean of two or more series of measurements, and in some instances of the blood of different individuals of the species. The powers employed were usually 1150 and 2300 diameters. To our own measurements we have added the corresponding results, with some additional, of Prof. Gulliver, from his very extended measurements as published in the *Proceedings of the Zoological Society of London*, June 15, 1875; and also in *Hewson's Works*, p. 237 *et seq.*

Average Size of the Red Blood-Corpuscles.

Mammals.	Wormley.	Gulliver.	Mammals.	Wormley.	Gulliver.
Man	1–3250	1–3200	Rhinoceros	1–3649	1–3765
Monkey	1–3382	1–3412	Tapir	1–4175	1–4000
Opossum	1–3145	1–3557	Lion	1–4143	1–4322
Guinea-pig	1–3223	1–3538	Ocelot	1–3885	1–4220
Kangaroo	1–3410	1–3440	Mule	1–3760	
Musk-rat	1–3282	1–3550	Ass	1–3620	1–4000
Dog	1–3561	1–3532	Ground-squirrel	1–4200	
Rabbit	1–3653	1–3607	Bat	1–3966	1–4175
Rat	1–3652	1–3754	Sheep	1–4912	1–5300
Mouse	1–3743	1–3814	Ibex	1–6445	
Pig	1–4268	1–4230	Goat	1–6189	1–6366
Ox	1–4219	1–4267	Sloth	. . .	1–2865
Horse	1–4243	1–4600	Platypus (duck-billed)	. . .	1–3000
Cat	1–4372	1–4404	Whale	. . .	1–3099
Elk	1–4384	1–3938	Capybara	1–3164	1–3190
Buffalo	1–4351	1–4586	Seal	. . .	1–3281
Wolf (prairie)	1–3422	1–3600	Woodchuck	. . .	1–3484
Bear (black)	1–3656	1–3693	Musk-deer	. . .	1–12325
Hyena	1–3644	1–3735	Beaver	. . .	1–3325
Squirrel (red)	1–4140	1–4000	Porcupine	. . .	1–3369
Raccoon	1–4084	1–3950	Llama { long diam.	1–3201	1–3361
Elephant	1–2738	1–2745	Llama { short "	1–6408	1–6229
Leopard	1–4390	1–4319	Camel { long diam.	1–3331	1–3123
Hippopotamus	1–3560	1–3429	Camel { short "	1–5280	1–5876

Birds.	Wormley.		Gulliver.	
	Length.	Breadth.	Length.	Breadth.
Chicken	1–2080	1–3483	1–2102	1–3466
Turkey	1–1894	1–3444	1–2045	1–3598
Duck	1–1955	1–3504	1–1937	1–3424
Pigeon	1–1892	1–3804	1–1973	1–3643
Goose	. . .	. . .	1–1836	1–3839
Quail	. . .	. . .	1–2347	1–3470
Dove	. . .	. . .	1–2005	1–3369
Sparrow	. . .	. . .	1–2140	1–3500
Owl	. . .	. . .	1–1763	1–4076

Reptiles.	Wormley.		Gulliver.	
	Length.	Breadth.	Length.	Breadth.
Tortoise (land)	1–1250	1–2200	1–1252	1–2216
Turtle (green)	. . .	. . .	1–1231	1–1882
Boa-constrictor	1–1245	1–2538	1–1440	1–2400
Viper	. . .	. . .	1–1274	1–1800
Lizard	. . .	. . .	1–1555	1–2743

Batrachians.	Wormley.		Gulliver.	
	Length.	Breadth.	Length.	Breadth.
Frog	1–1089	1–1801	1–1108	1–1821
Toad	. . .	. . .	1–1043	1–2000
Triton	. . .	. . .	1–848	1–1280
Proteus	. . .	. . .	1–400	1–727
Amphiuma tridactylum	1–358	1–622	1–363	1–615

Fishes.	Gulliver.	
	Length.	Breadth.
Trout	1–1524	1–2460
Perch	1–2099	1–2824
Pike	1–2000	1–3555
Eel	1–1745	1–2842
Lamprey	Circular.	1–2134
Nucleus	. . .	1–6400

On comparing the foregoing results of Prof. Gulliver and our own, it is seen that the greatest difference is in the blood of the opossum (*Didelphys Virginiana*), in which the difference between the averages is 1–27,152d of an inch. Not only in respect to size, according to our own measurements, are the corpuscles of the opossum closely allied to those of man, but they also present that peculiar bright appearance, or "stamp of individuality," as Prof. Johnston expresses it (*Microscopy of the Blood, Transactions International Medical Congress*, 1876, 479), observed in human corpuscles. This same peculiarity is also strongly marked in the blood-corpuscles of the kangaroo.

The next greatest difference, in the above measurements, occurs in the blood of the guinea-pig, in which it is 1–36,200th of an inch. However, the species of animal examined by Prof. Gulliver was

the *Cavia cobaya*, whilst that which we examined was the *Cavia aperea*. Our average of 1–3223d of an inch is based on the measurement of three hundred corpuscles of the same animal. The mean diameter of four hundred corpuscles of a like animal measured by Dr. J. J. Woodward (*Louisville Med. Jour.*, Aug. 1876, 120) was 1–3213th of an inch.

With the exceptions now stated, and some three or four others of minor extent, the results of the foregoing series of measurements are practically identical. From repeated measurements of the blood of the dog, Dr. J. J. Woodward concluded that the corpuscles of this animal were more closely allied in size to those of man than is usually stated by writers, and that these bloods might thus readily be confounded, even in their fresh state. (*Amer. Jour. Med. Sci.*, Jan. 1875, 151; and *Louisville Med. Jour.*, Aug. 1876, 121.) Our own average of the blood of the dog is based on the examination of the blood of a number of animals differing much in size and variety, the results in each case being closely concordant.

The *apparent* size, under a power of 1150 diameters, of the prevailing corpuscles of six different bloods, embracing the principal range of mammalian blood, is shown in Plate XVI. It will there be seen that under this power corpuscles differing in diameter by the 1–100,000th of an inch are readily discriminated. The corpuscles as they appeared to the eye under a simple lens amplifying 184 times were figured by Hewson, he representing those of man, the dog, and the rabbit of the same size, and those of the ox, cat, mouse, ass, and bat of equal size. (*Hewson's Works*, 217.)

From a series of microscopic measurements of the blood-corpuscles, C. Schmidt, in 1848, claimed that in this manner the blood of many of the mammalia could be distinguished from that of man and he proposed the method for the diagnosis of suspected stains in criminal cases. His measurements were made with a power of 500 diameters, and in each blood he took the average of forty corpuscles. His results correspond for the most part quite closely with the measurements already given.

Limit of Discrimination.—The difference thus found to exist in the average size of the corpuscles of mammalian blood enables the microscopist to discriminate readily the blood of certain animals, including man, from that of certain other animals of this class, especially when, as strongly advised by Dr. J. G. Richardson

(*Amer. Jour. Med. Sci.*, July, 1874, 102), the higher powers of the instrument are employed.

Thus, for example, if it were claimed, as in a case some years since, that a blood was that of a rabbit, and under examination the corpuscles were found to have an average diameter of about 1–3300th of an inch, it would be quite certain that the blood was *not* that of a rabbit. But the fact that the corpuscles had a mean diameter of about 1–3300th of an inch would not in itself *prove* that the blood was that of man, since the result would be equally consistent with the blood of several different animals. So, on the other hand, if the mean diameter of the corpuscles was found to be about 1–3700th of an inch, this fact alone would not prove that the blood was that of a rabbit, since it might be that of certain other animals, or even, under certain conditions, the blood of man. How far a discrimination of this kind could in any given case be safely carried would depend much upon the number and the range in size of the corpuscles measured.

This difficulty of individualization arises from the fact, as we have already seen, that the average diameters of the corpuscles of the different mammals are in many instances at least practically the same, and these averages, for the most part, pass by imperceptible gradations throughout the entire class. Thus, virtually of the same size as the corpuscles of man are at least those of the guinea-pig, musk-rat, seal, beaver, opossum, and capybara, whilst those of certain other animals are but slightly larger and might be reduced in size to those of man.

Hence, then, *the microscope may enable us to determine with great certainty that a blood is* NOT *that of a certain animal and is* CONSISTENT *with the blood of man; but in no instance does it, in itself, enable us to say that the blood is really human, or indicate from what particular species of animal it was derived.*

There seems to be much misunderstanding as to the true value of this instrument in investigations of this kind, it being regarded by some as nearly or altogether useless for this purpose, whilst others claim for it results wholly at variance with the facts in the case. This, like many other tests, has its fallacies, and if these, in a given case, cannot be reasonably met, the accused should have the benefit of the doubt.

V. Examination of Dried Blood.

For the recovery of the *blood-corpuscles* from dried stains and coagula various solutions and liquids have been advised. Of these may be mentioned sodium chloride and sulphate, potassium iodide, arsenious acid, corrosive sublimate, and diluted glycerine. So, also, Moleschott recommended a 33 per cent. solution of potassium hydrate; and Prof. Rednew, of St. Petersburg, a solution of two parts of potassium dichromate with one part of sodium sulphate in one hundred parts of water. Pacini's fluid, which has been highly extolled for this purpose, consists of a mixture of common salt, corrosive sublimate, glycerine, and water.

After considerable experience with most of these liquids for this purpose, and others, side by side with *pure water*, we prefer, at least in most instances, the latter fluid, added in quantity not to exceed the proportion present in normal blood. A solution of glycerine, of sp. gr. 1030, generally answers the purpose very well, and has the advantage of not evaporating as readily as pure water. When the stain is quite old, the addition of a little potassium hydrate may much facilitate the disintegration of the mass.

For the examination it is much more satisfactory, as already stated, to have a dried clot, even if exceedingly minute, than to employ a portion of stained fabric. Even in only a minute stain a clot may generally be found by examining it under a simple lens. Any clot thus found is placed on a glass slide, gently crushed, moistened with a small drop of water, then covered with a thin glass and examined in the usual manner. In the absence of a clot, the scrapings or a few fibres of the stained fabric are examined in a similar manner.

When the stain is at least comparatively fresh, the corpuscles may manifest themselves very quickly; whilst if the mass is old, it may require some hours for disintegration. In this respect, however, great differences may be observed even in stains of the same age. The breaking up of the mass is sometimes much hastened by gently moving the glass cover. When the corpuscles are slow to separate, it is more satisfactory to watch the disintegration under a medium power, as a one-fifth inch objective, and as they appear measure them under a higher power. A very good method of examining old stains is to place the moistened clot on the thin glass and then invert this over a glass slide having a slightly concaved centre.

If, during the examination, any of the corpuscles become entirely decolorized and spherical in form, they should not be included in the measurements, since they are obviously no longer normal. Some of the corpuscles, as already mentioned, resist the action of water much more than others. In fact, these are the corpuscles generally seen in examinations of this kind.

Experiments.—In order to ascertain how far the blood-corpuscles of different animals might be recovered of their normal size from dried blood after various periods, the following examinations were made, the dried blood being either in the form of a stain on muslin or as dried coagula that had been loosely preserved in paper. To these average measurements are added those of the corresponding blood as obtained from the fresh fluid, or the blood after drying in thin layers on a glass slide. In every instance, save one, not less than forty corpuscles were measured.

Examination of Old Blood-Stains.

Animal.	Age of Stain.	Remarks.	Average.	Fresh Blood.
(1) Human . .	2 months old.	Stain, unknown.	1–3358th inch.	1–3250th inch.
(2) " . .	2½ " "	Stain.	1–3236th "	" "
(3) " . .	3 " "	"	1–3384th "	" "
(4) " . .	19 " "	Clot.	1–3290th "	" "
(5) Elephant . .	13 " "	"	1–2849th "	1–2738th "
(6) Dog . . .	4 " "	Trace of stain, unknown.	1–3626th "	1–3561st "
(7) Rabbit . .	18 " "	Clot.	1–3683d "	1–3653d "
(8) Ox	16 " "	Stain.	1–4544th "	1–4219th "
(9) "	32 " "	Stain, unknown.	1–4495th "	" "
(10) "	4½ years "	Clot.	1–4535th "	" "
(11) Buffalo . .	18 months "	"	1–4312th "	1–4351st "
(12) Goat . . .	17 " "	Stain.	1–5897th "	1–6189th "
(13) Ibex . . .	18 " "	Clot.	1–6578th "	1–6445th "

In the case of the human blood, No. 1, two months old, the deposit was in the form of a thin stain on muslin, and its nature, other than that it was mammalian blood, was unknown at the time of examination. The corpuscles were readily found, and two series of thirty corpuscles each were measured. In the human blood two and a half months old, fifty corpuscles, ranging from 1–3125th to 1–3448th of an inch, were measured.

The blood-stain of the dog, No. 6, was prepared by Dr. Frankenberg, and consisted of a single stain so minute as to be barely visible to the naked eye: its nature at the time of the examination was unknown. In this instance only fifteen corpuscles were measured.

In the ox blood four and half years old, the corpuscles were rather readily obtained, and two closely concordant series of measurements were made.

In examinations of this kind it should be borne in mind that certain portions of a deposit may fail to yield satisfactory results, whilst from other portions the corpuscles may be readily obtained.

Cases.—In a case of murder in which we were consulted some years since (*State of Ohio* v. *John Barckley*), upon the pantaloons of the prisoner a stain that apparently had been washed was found; but the linen of the pocket immediately under the stain exhibited a marked stain, from which minute clots were obtained. These readily revealed the presence of blood-corpuscles ranging in diameter from 1–3030th to 1–3600th of an inch, the average being 1–3242d of an inch. Before execution the prisoner admitted that he had hastily washed the stain with water from a small stream near which the murder was committed.

In another case, it was claimed that some spots upon a hat were made by the blood of a turkey, and was so testified by two associates of the accused. The blood, however, was clearly that of a mammal, and was quite consistent with that of the human subject. In both these instances the examination was made within a few days after the stain was received.

In a case tried a few years since, the clothes of the accused presented a great number of stains, some of which were quite large, which he claimed were due to the slaughter of sheep, his statement in regard to killing sheep being confirmed by several witnesses. A closer examination of the clothes, however, indicated a somewhat marked difference between certain of the stains, and independent examinations by three different observers showed that while some of the stains contained blood-corpuscles quite consistent with those of the sheep, others contained corpuscles wholly inconsistent with those of that animal, but quite consistent with human blood.

Fallacies.—In the examination of suspected stains the examiner should bear in mind the possible presence of vegetable spores, which in appearance and size may closely resemble blood-corpuscles. Two instances of this kind have come within our own personal knowledge.

In one of these, minute circular bodies were found in very great numbers in a suspected pail partly filled with water, and, as many of the bodies had a diameter of about 1–3300th of an inch, they were pronounced human blood-corpuscles. A subsequent and independent examination, however, proved them to be simply the sporules of a confervoid algæ.

In a more recent case, similar spores, found in a suspected deposit upon a rock, were at first mistaken for blood-corpuscles; but a subsequent examination convinced the observer that he was in error.

Gorup-Besanez cites a similar case (*Phys. Chem.*, 1867, 350), where an earth which from its red color appeared strongly saturated with blood was found on microscopic examination by Prof. Erdmann to contain circular bodies which at first might readily be mistaken for blood-corpuscles, but which were really the spores of the algæ *Porphyridium cruentum*.

The general character and appearance of spores of this kind, when more carefully examined, will in most instances readily distinguish them from blood-corpuscles; they usually vary much more in size than the corpuscles of any single blood: in respect to size, however, they may be pretty uniform. Under the action of water they generally remain unchanged in appearance; whereas blood-corpuscles become transparent and, at least for the most part, disappear from view. It need hardly be stated that vegetable spores have not the chemical and optical properties of blood-corpuscles.

Location of Stains.—Not only should all stains of this kind be accurately located upon the article on which they are found, but it is sometimes of very great importance to determine upon which *side* of the fabric they were received. For determinations of this kind the binocular microscope, with a low power, will sometimes be found very useful. The following very remarkable case (*State of Ohio* v. *Amelia Richardson*, 1876), in which this question was involved, may be briefly cited.

Two pistol-shots were heard shortly after midnight, at an interval of several minutes or more. A few minutes after the second shot an officer entered the room from which the report proceeded. He found a man lying on the floor on the left side of the bed, dead, with a pistol-ball wound in his head and blood oozing from the wound upon the carpet. The wife of the dead man was bleeding from an incised wound in the throat, and was also wounded, apparently by a ball, in the loose flesh upon her side, upon which there were two apertures near each other.

The woman stated that while asleep her husband attempted to cut her throat with a razor, which she wrested from him. He then shot her in the side, after which she obtained the pistol and shot him in self-defence. In confirmation of her statement she pointed to blood-stains on the upper portion of the sheet on the *right* side of the bed, which side she claimed she occupied when she received the wound in her throat.

On carefully examining these stains, they were readily found to consist of blood. But on one side of the sheet the stains were much more marked than on the other, and they contained many small clots; whilst on the least stained side there were but few clots, and these were very minute; further, portions of the stains at their edges, on the most strongly marked side of the sheet, did not fully extend through the fabric. These appearances, with other facts, seemed clearly to indicate that the blood was received on the side of the sheet on which the stains were most marked. This proved to be the *under* side of the lower sheet as found on the bed.

At the trial of the case, the State held that the woman first shot her husband upon the left side of the bed, and that his body then fell or was put upon the floor, and that the sheet which was thus stained was then reversed so as to bring the stains upon her side of the bed. Several surgeons testified that in their opinion the wound on the throat of the woman was self-inflicted, and that when the ball was received upon her side the skin was folded and distended. There was strong reason to believe she had an accomplice, who escaped from the house as the officer entered. The woman was found guilty of murder in the second degree.

Blood in Insects.—The singular observation has been made by M. Curtmann that when blood-sucking insects are killed stains may result in which human blood-corpuscles are plainly recognizable. Human blood, he states, is more rapidly digested by bugs than by mosquitoes, since it is not detected in the former after twelve hours, while in the latter it may be found even later than twenty-four hours after the ingestion of the blood.

PLATE I.

FIG. 1. $\frac{1}{100}$ grain POTASSIUM OXIDE, as nitrate or chloride, + *Platinic Chloride*, × 225 diameters.

" 2. $\frac{1}{100}$ grain POTASSIUM OXIDE, as nitrate, + *Tartaric Acid*, × 100 diameters.

" 3. $\frac{1}{250}$ grain POTASSIUM OXIDE, as chloride, + *Sodium Tartrate*, × 80 diameters.

" 4. $\frac{1}{200}$ grain POTASSIUM OXIDE, as nitrate, + *Picric Acid*, × 40 diameters.

" 5. $\frac{1}{100}$ grain AMMONIA, as ammonium chloride, + *Picric Acid*, × 40 diameters.

" 6. $\frac{1}{25}$ grain SODIUM OXIDE, + *Picric Acid*, × 40 diameters.

Fig. 1

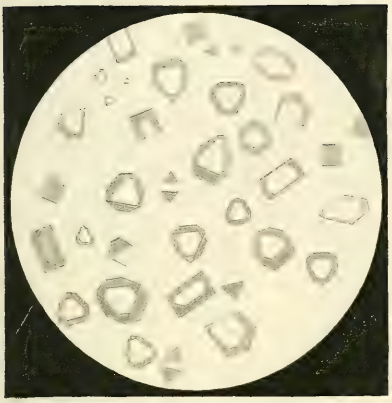


Fig. 2.

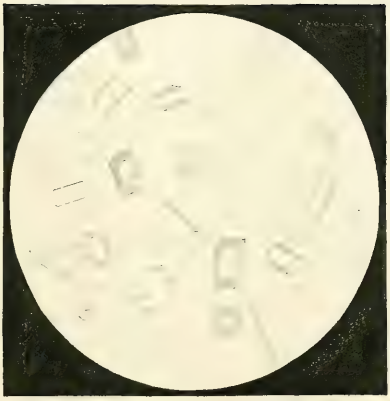


Fig. 3.

Fig. 4.

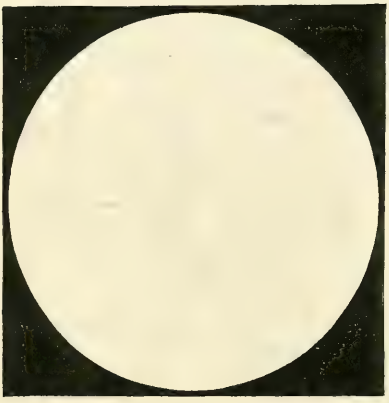


Fig. 5.

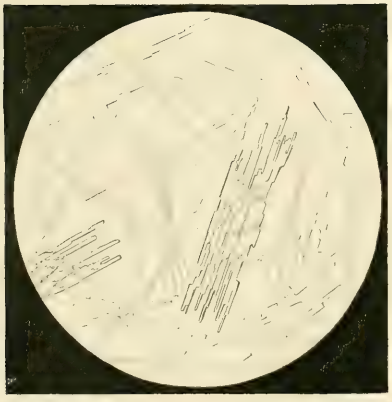


Fig. 6.

PLATE II.

FIG. 1. $\frac{1}{25}-\frac{1}{100}$ grain SODIUM OXIDE, + *Potassium Metantimoniate*, × 100 diameters.

" 2. $\frac{1}{10}$ grain SODIUM OXIDE, + *Tartaric Acid*, × 40 diameters.

" 3. $\frac{1}{1000}$ grain SODIUM OXIDE, as chloride, + *Platinic Chloride*, × 40 diameters.

" 4. $\frac{1}{100}$ grain SULPHURIC ACID, + *Barium Chloride*, × 100 diameters.

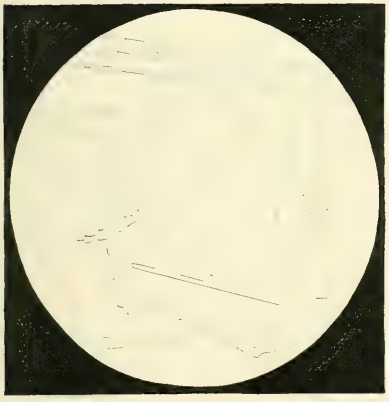
" 5. HYDROFLUOSILICIC ACID, + *Barium Chloride*, × 100 diameters.

" 6. $\frac{1}{100}$ grain SULPHURIC ACID, + *Strontium Nitrate*, × 75 diameters.

Fig. 1

Fig. 2

Fig. 3.



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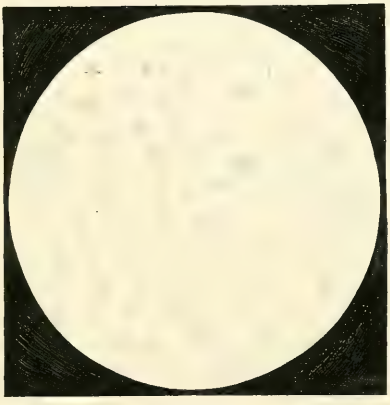


Fig. 5.

Fig. 6

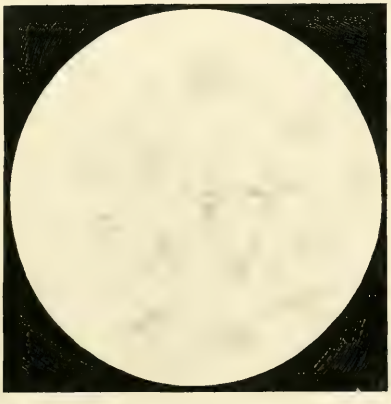


PLATE III.

FIG. 1. $\frac{1}{100}$ grain HYDROCHLORIC ACID, + *Lead Acetate*, × 40 diameters.

" 2. $\frac{1}{1000}$ grain OXALIC ACID, on spontaneous evaporation, × 80 diameters.

" 3. $\frac{1}{1000}$ grain OXALIC ACID, + *Calcium Chloride*, × 225 diameters.

" 4. $\frac{1}{100}$ grain OXALIC ACID, + *Barium Chloride*, × 80 diameters.

" 5. $\frac{1}{100}$ grain OXALIC ACID, + *Strontium Nitrate*, × 125 diameters.

" 6. $\frac{1}{500}$ grain OXALIC ACID, + *Lead Acetate*, × 80 diameters.

Fig. 1.

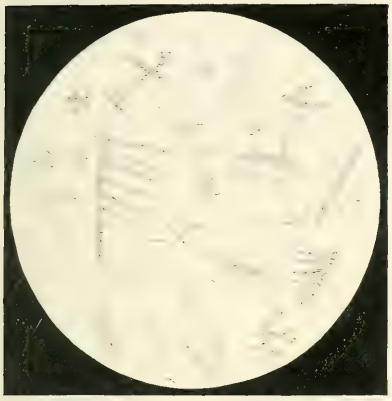
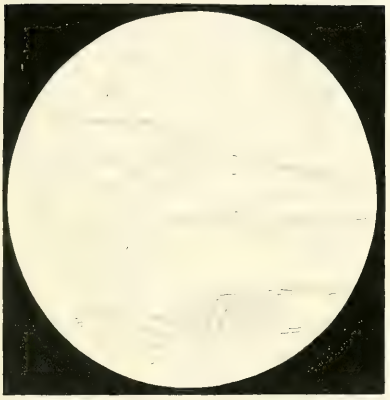


Fig. 2.



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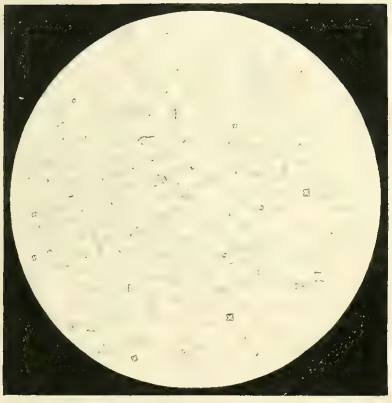

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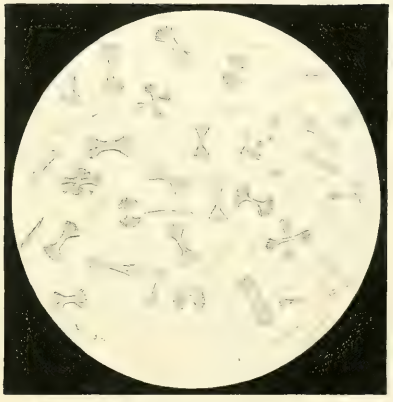

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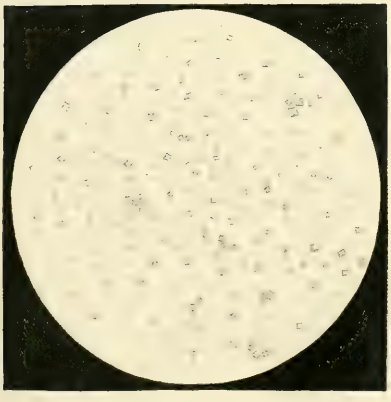


Fig. 6.

PLATE IV.

FIG. 1. $\frac{1}{10000}$ grain HYDROCYANIC ACID vapor, + *Silver Nitrate*, × 225 diameters.

" 2. $\frac{1}{100000}$ grain HYDROCYANIC ACID vapor, + *Silver Nitrate*, × 125 diameters.

" 3. $\frac{1}{1000}$ grain PHOSPHORIC ACID, + *Ammonium Magnesium Sulphate*, × 80 diameters.

" 4. TARTAR EMETIC, from hot supersaturated solution, × 40 diameters.

" 5. ARSENIOUS OXIDE, sublimed, × 125 diameters.

" 6. $\frac{1}{100}$ grain ARSENIOUS OXIDE, + *Ammonium Silver Nitrate*, × 75 diameters.

Fig. 1

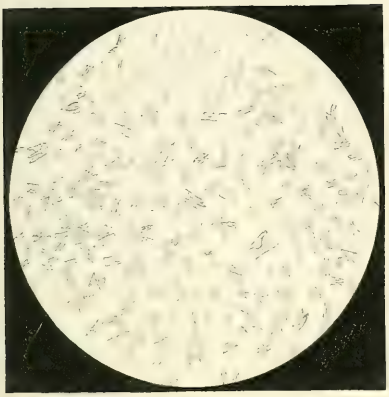


Fig. 2

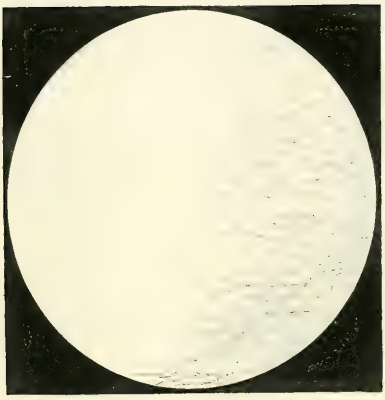
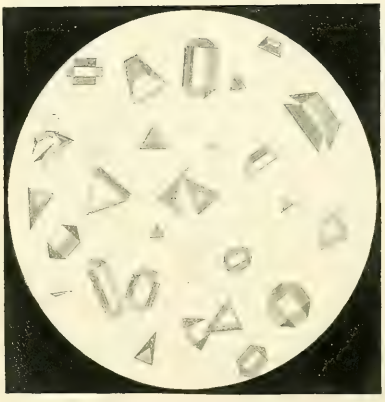


Fig. 3

Fig. 4



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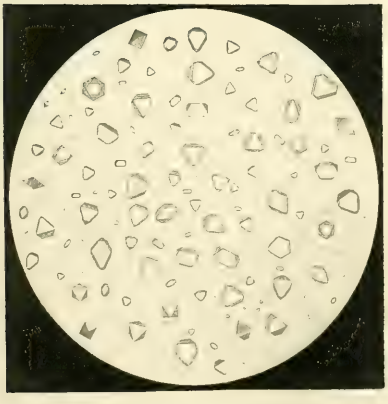


Fig. 6.

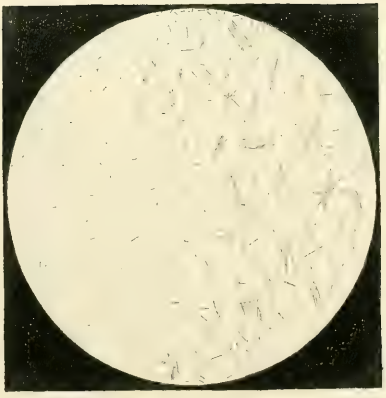


PLATE V.

FIG. 1. $\frac{1}{100}$ grain ARSENIC OXIDE, + *Ammonium Magnesium Sulphate*, × 75 diameters.

" 2. CORROSIVE SUBLIMATE, sublimed, × 40 diameters.

" 3. $\frac{1}{100}$ grain LEAD, + diluted *Sulphuric Acid*, × 80 diameters.

" 4. $\frac{1}{100}$ grain LEAD, + diluted *Hydrochloric Acid*, × 80 diameters.

" 5. $\frac{1}{2500}$ grain LEAD, + *Potassium Iodide*, × 80 diameters.

" 6. $\frac{1}{1000}$ grain ZINC, + *Oxalic Acid*, × 80 diameters.

Fig. 1

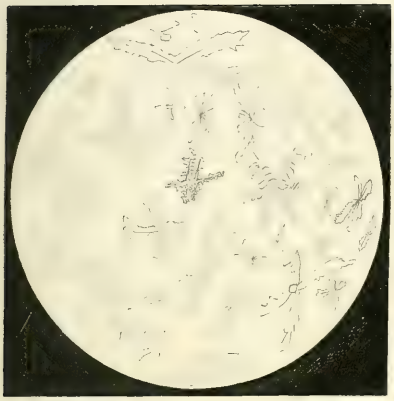


Fig. 2

Fig. 3

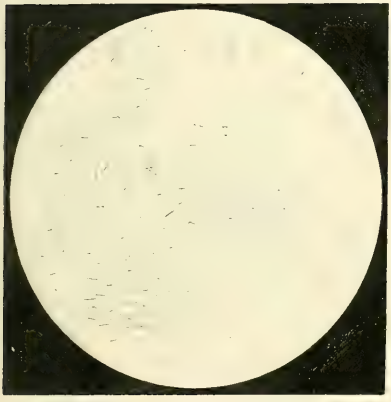


Fig. 4

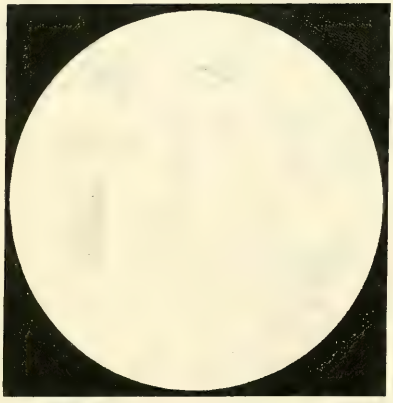


Fig. 5

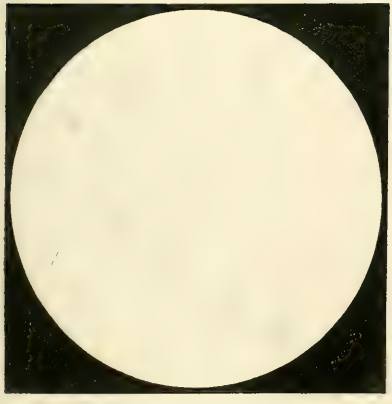


Fig. 6

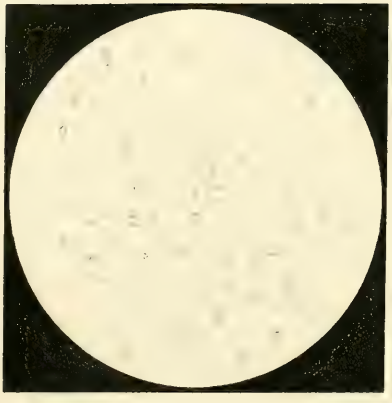


PLATE VI.

FIG. 1. $\frac{1}{100}$ grain NICOTINE, + *Platinic Chloride*, × 40 diameters.

" 2. $\frac{1}{100}$ grain NICOTINE, + *Corrosive Sublimate*, × 40 diameters.

" 3. $\frac{1}{1000}$ grain NICOTINE, + *Picric Acid*, × 40 diameters.

" 4. CONINE, pure, + vapor of *Hydrochloric Acid*, × 40 diameters.

" 5. $\frac{1}{100}$ grain CONINE, + *Picric Acid*, × 40 diameters.

" 6. $\frac{1}{100}$ grain MORPHINE, + *Potassium Hydrate*, × 40 diameters.

Fig. 1.

Fig. 2.

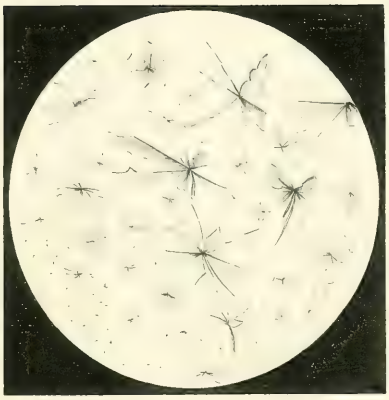
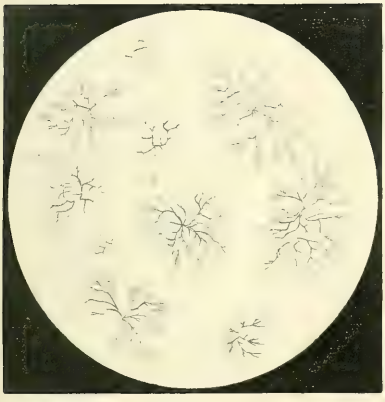


Fig. 3.



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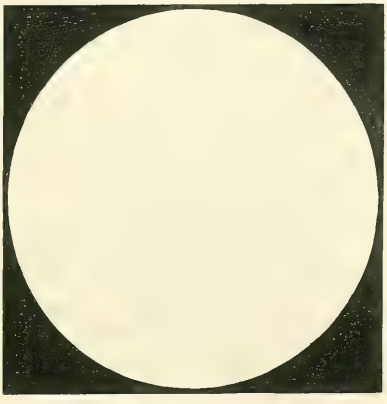


Fig. 5.

Fig. 6.

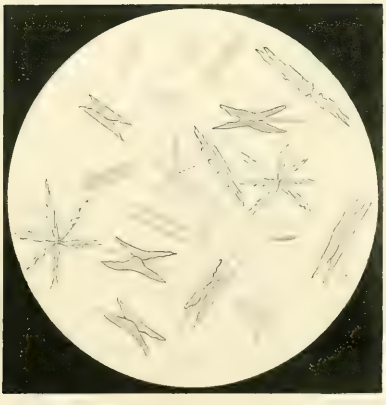


PLATE VII.

FIG. 1. $\frac{1}{100}$ grain MORPHINE, + *Potassium Iodide*, $\times$ 40 diameters.

" 2. $\frac{1}{100}$ grain MORPHINE, + *Potassium Chromate*, $\times$ 80 diameters.

" 3. $\frac{1}{100}$ grain MORPHINE, + *Platinic Chloride*, $\times$ 80 diameters.

" 4. $\frac{1}{100}$ grain MECONIC ACID, + *Barium Chloride*, $\times$ 80 diameters.

" 5. $\frac{1}{100}$ grain MECONIC ACID, + *Hydrochloric Acid*, $\times$ 75 diameters.

" 6. $\frac{1}{100}$ grain MECONIC ACID, + *Potassium Ferricyanide*, $\times$ 40 diameters.

Fig. 1.

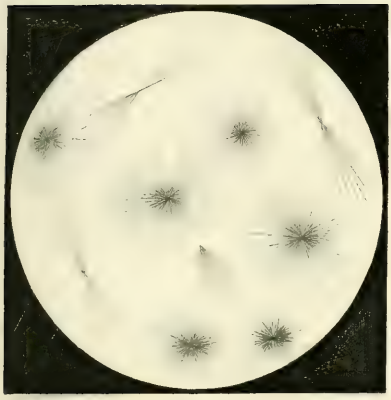


Fig. 2.

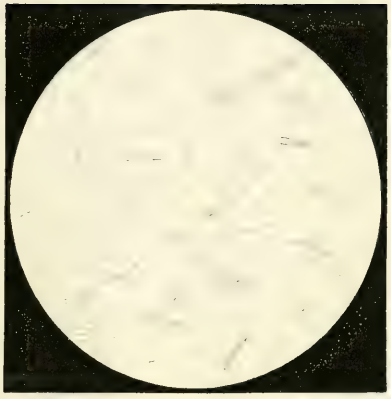


Fig. 3.

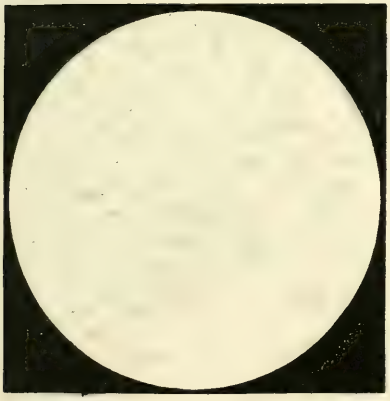
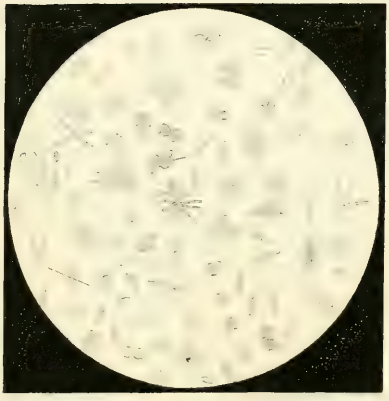


Fig. 4.



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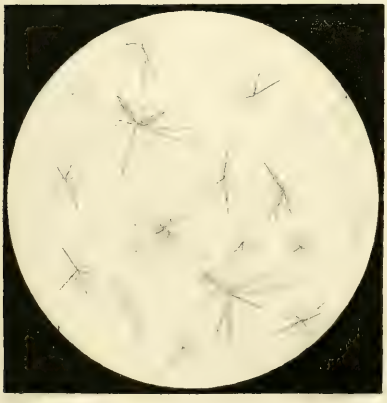


Fig. 6.

PLATE VIII.

FIG. 1. $\frac{1}{100}$ grain MECONIC ACID, + *Calcium Chloride*, × 75 diameters.

" 2. $\frac{1}{1000}$ grain NARCOTINE, + *Potassium Hydrate*, × 40 diameters.

" 3. $\frac{1}{100}$ grain NARCOTINE, + *Potassium Acetate*, × 80 diameters.

" 4. $\frac{1}{100}$ grain CODEINE, + *Iodine in Potassium Iodide*, × 40 diameters.

" 5. $\frac{1}{100}$ grain CODEINE IODIDE, from alcoholic solution, × 75 diameters.

" 6. $\frac{1}{100}$ grain CODEINE, + *Potassium Sulphocyanide*, × 40 diameters.

Fig. 1

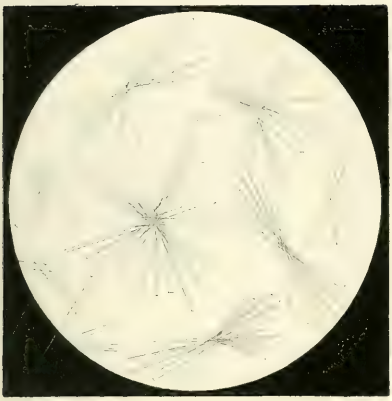


Fig. 2

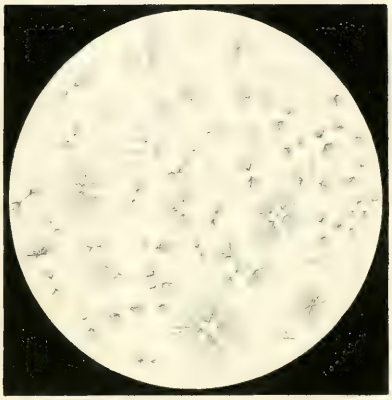


Fig. 3.

Fig. 4.

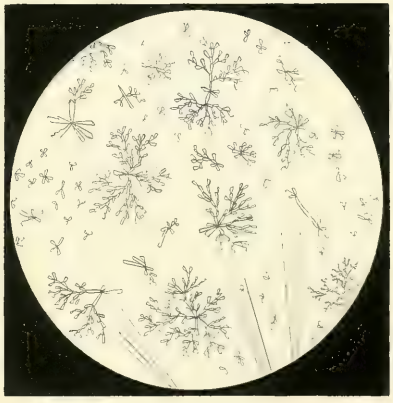


Fig. 5.

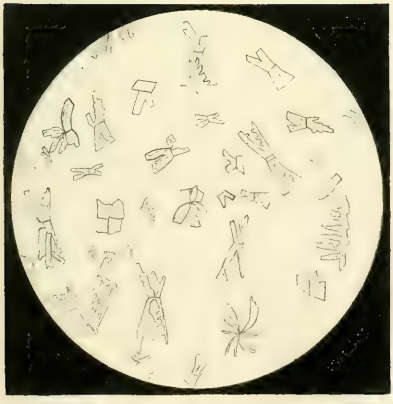


Fig. 6.

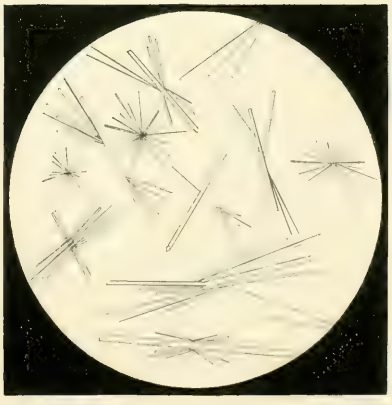


PLATE IX.

FIG. 1. $\frac{1}{100}$ grain CODEINE, + *Potassium Dichromate*, × 40 diameters.

" 2. $\frac{1}{100}$ grain CODEINE, + *Potassium Iodide*, × 40 diameters.

" 3. $\frac{1}{1000}$ grain NARCEINE, + *Iodine in Potassium Iodide*, × 40 diameters.

" 4. $\frac{1}{500}$ grain NARCEINE, + *Potassium Dichromate*, × 40 diameters.

" 5. $\frac{1}{500}$ grain OPIANYL, + *Iodine in Potassium Iodide*, × 40 diameters.

" 6. $\frac{1}{500}$ grain OPIANYL, + *Bromine in Bromohydric Acid*, × 40 diameters.

Fig. 1.

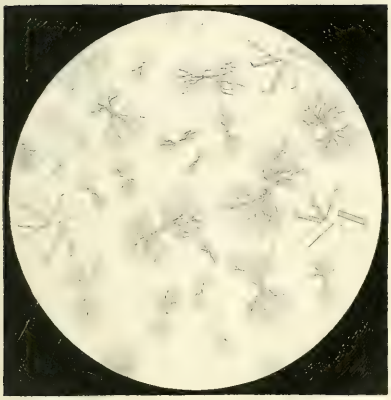


Fig. 2.

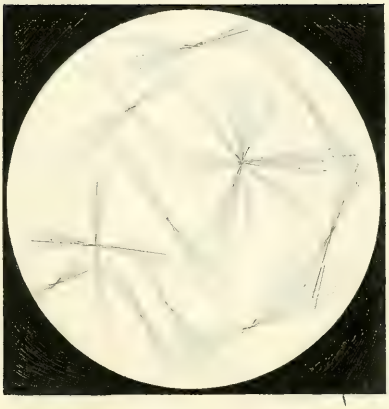


Fig. 3.

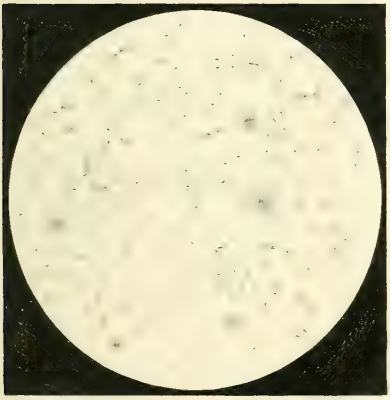


Fig. 4.

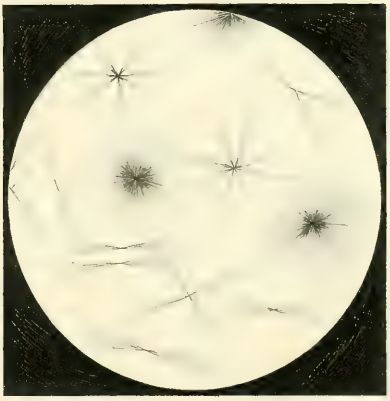


Fig. 5.

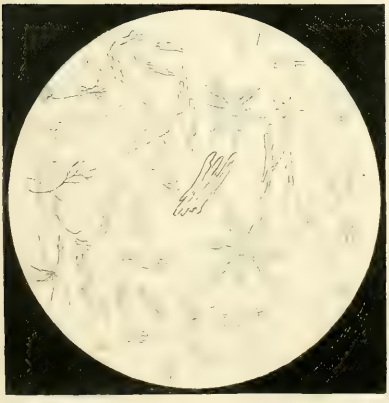


Fig. 6.

PLATE X.

FIG. 1. $\frac{1}{100}$ grain STRYCHNINE, + *Potassium Hydrate or Ammonia*, × 40 diameters.

" 2. $\frac{1}{100}$ grain STRYCHNINE, + *Potassium Sulphocyanide*, × 40 diameters.

" 3. $\frac{1}{500}$ grain STRYCHNINE, + *Potassium Dichromate*, × 40 diameters.

" 4. $\frac{1}{2500}$ grain STRYCHNINE, + *Potassium Dichromate*, × 80 diameters.

" 5. $\frac{1}{1000}$ grain STRYCHNINE, + *Auric Chloride*, × 40 diameters.

" 6. $\frac{1}{1000}$ grain STRYCHNINE, + *Platinic Chloride*, × 40 diameters.

Fig. 1.

Fig. 2.

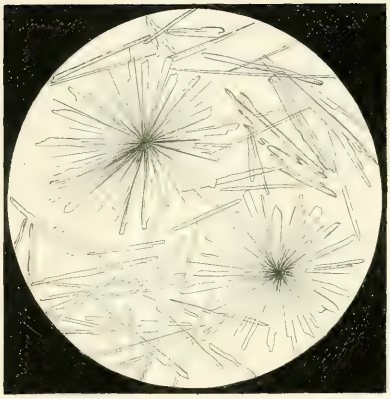


Fig. 3.

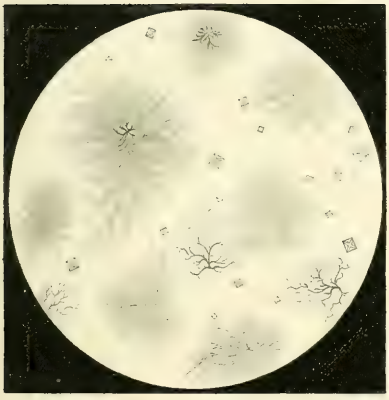


Fig. 4.

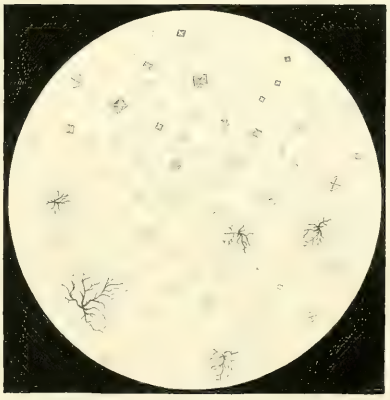


Fig. 5.

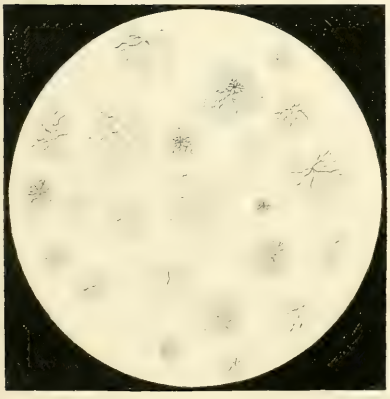


Fig. 6.

PLATE XI.

FIG. 1. $\frac{1}{1000}$ grain STRYCHNINE, + *Picric Acid*, × 80 diameters.

" 2. $\frac{1}{100}$ grain STRYCHNINE, + *Corrosive Sublimate*, × 40 diameters.

" 3. $\frac{1}{100}$ grain STRYCHNINE, + *Potassium Ferricyanide*, × 40 diameters.

" 4. $\frac{1}{1000}$ grain STRYCHNINE, + *Iodine in Potassium Iodide*, × 80 diameters.

" 5. $\frac{1}{100}$ grain BRUCINE, + *Potassium Hydrate or Ammonia*, × 40 diameters.

" 6. $\frac{1}{100}$ grain BRUCINE, + *Potassium Sulphocyanide*, × 40 diameters.

Fig. 1.

Fig. 2.

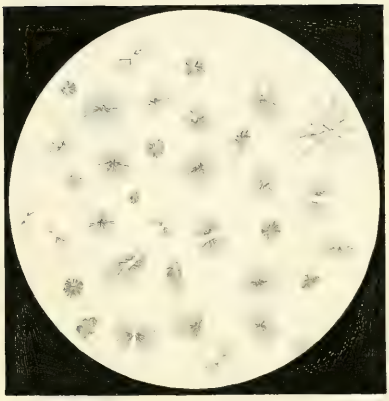


Fig. 3.

Fig. 4.

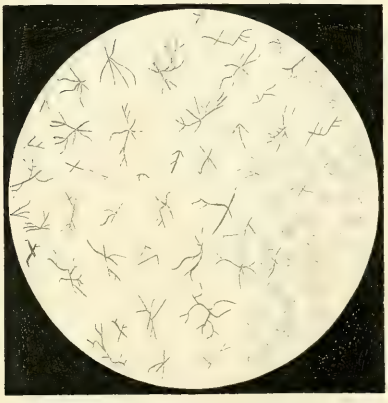


Fig. 5.

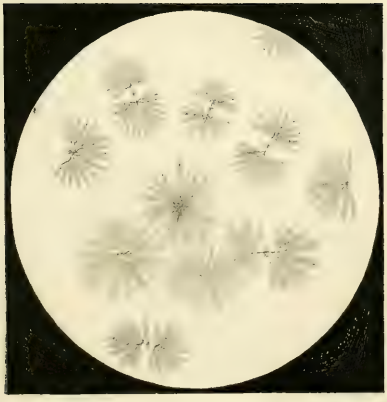


Fig. 6.

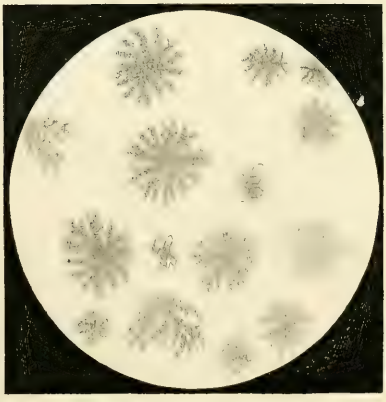


PLATE XII.

FIG. 1. $\frac{1}{100}$ grain BRUCINE, + *Potassium Dichromate*, × 80 diameters.

" 2. $\frac{1}{1000}$ grain BRUCINE, + *Platinic Chloride*, × 40 diameters.

" 3. $\frac{1}{100}$ grain BRUCINE, + *Potassium Ferricyanide*, × 40 diameters.

" 4. $\frac{1}{100}$ grain ATROPINE, + *Potassium Hydrate or Ammonia*, × 75 diameters.

" 5. $\frac{1}{100}$ grain ATROPINE, + *Bromine in Bromohydric Acid*, × 75 diameters.

" 6. $\frac{1}{10000}$ grain ATROPINE, + *Bromine in Bromohydric Acid*, × 125 diameters.

Fig. 1.

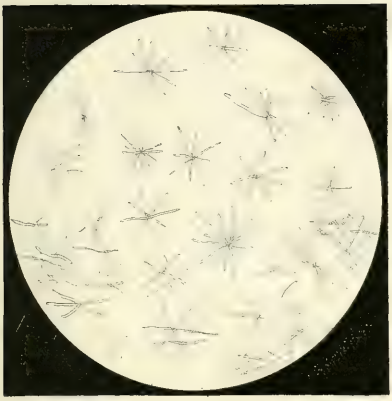


Fig. 2.

Fig. 3.

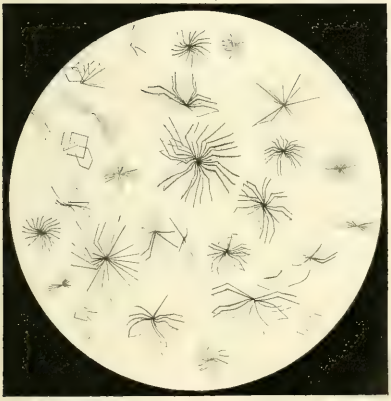


Fig. 4.

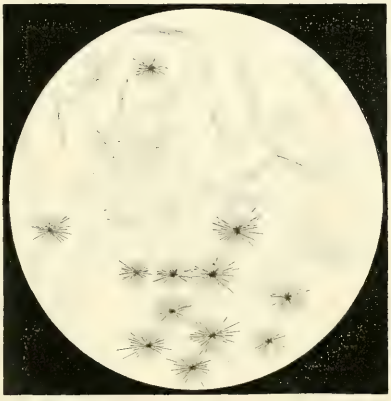


Fig. 5.

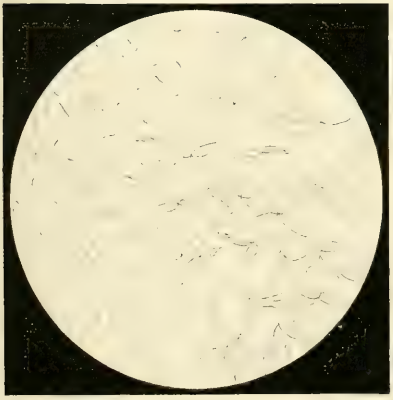


Fig. 6.

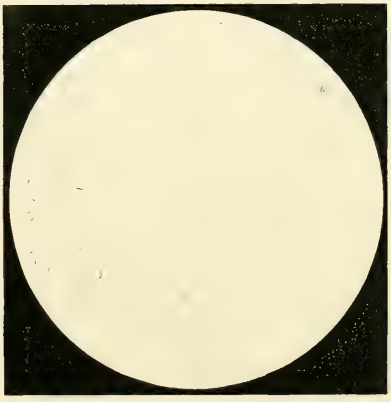


PLATE XIII.

FIG. 1. $\frac{1}{100}$ grain ATROPINE, + *Picric Acid*, × 80 diameters.

" 2. $\frac{1}{100}$ grain ATROPINE, + *Auric Chloride*, × 80 diameters.

" 3. $\frac{1}{100}$ grain VERATRINE, + *Auric Chloride*, × 40 diameters.

" 4. $\frac{1}{100}$ grain VERATRINE, + *Bromine in Bromohydric Acid*, × 80 diameters.

" 5. SOLANINE, from alcoholic solution, × 80 diameters.

" 6. $\frac{1}{100}$ grain SOLANINE, as sulphate, on spontaneous evaporation, × 80 diameters.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

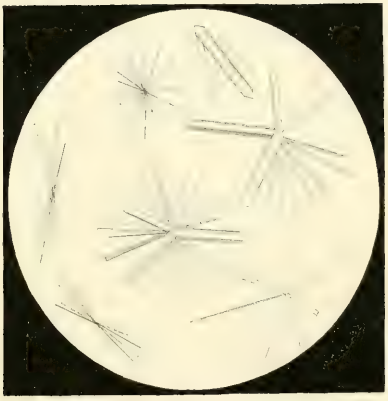


Fig. 5.

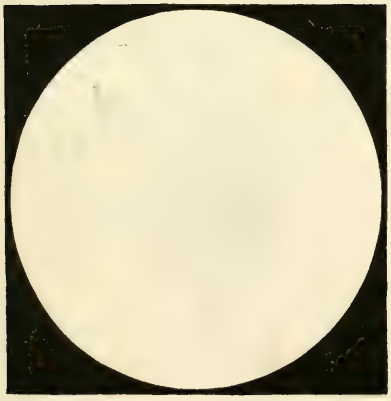


Fig. 6.

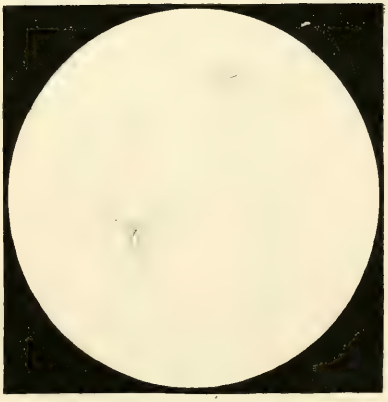


PLATE XIV.

FIG. 1. $\frac{1}{100}$ grain MORPHINE, + *Iodine in Potassium Iodide*, × 40 diameters.

" 2. $\frac{1}{1000}$ grain MORPHINE, + *Potassium Iodohydrargyrate*, × 40 diameters.

" 3. JERVINE, from ethereal solution, × 40 diameters.

" 4. $\frac{1}{100}$ grain JERVINE, + *Sulphuric Acid*, × 75 diameters.

" 5. $\frac{1}{100}$ grain JERVINE, + *Nitric Acid*, × 75 diameters.

" 6. JERVINE, from blood of cat, × 75 diameters.

Fig. 1.

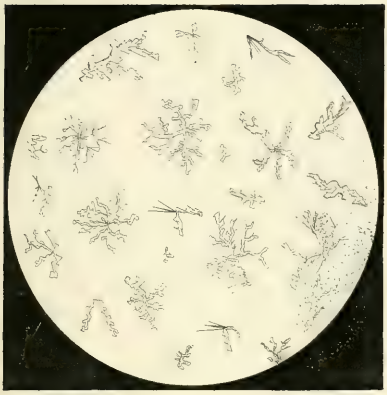


Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

PLATE XV.

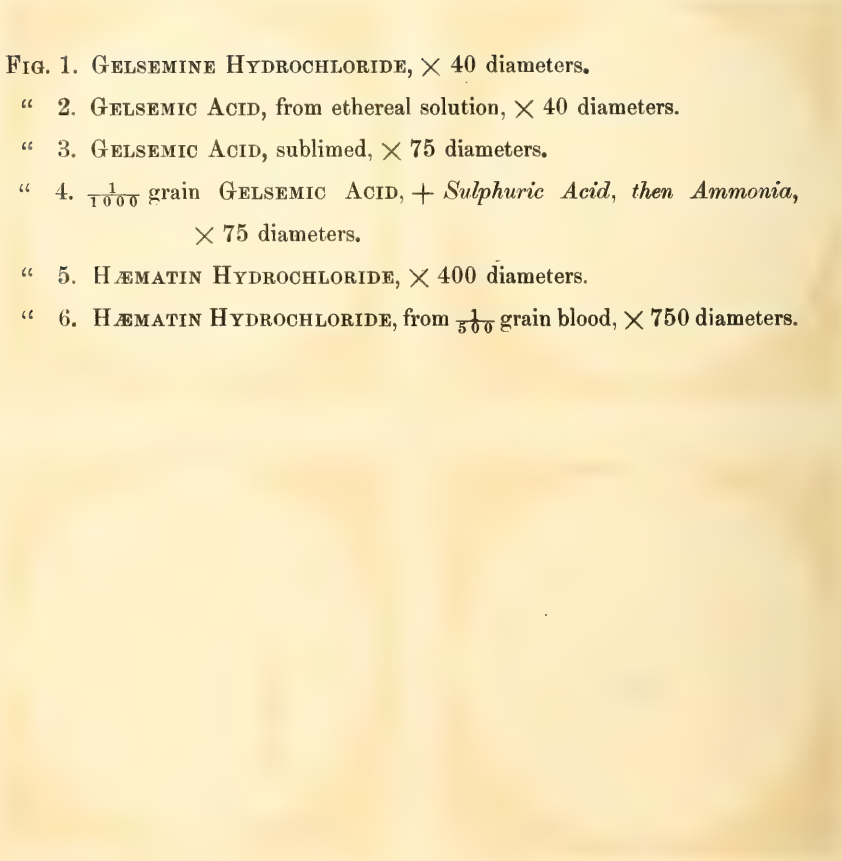


FIG. 1. GELSEMINE HYDROCHLORIDE, × 40 diameters.

" 2. GELSEMIC ACID, from ethereal solution, × 40 diameters.

" 3. GELSEMIC ACID, sublimed, × 75 diameters.

" 4. $\frac{1}{1000}$ grain GELSEMIC ACID, + *Sulphuric Acid, then Ammonia,* × 75 diameters.

" 5. HÆMATIN HYDROCHLORIDE, × 400 diameters.

" 6. HÆMATIN HYDROCHLORIDE, from $\frac{1}{500}$ grain blood, × 750 diameters.

Fig. 1.

Fig. 2.

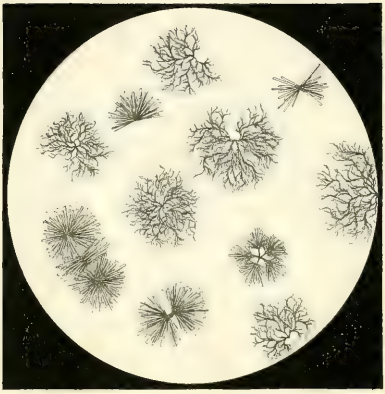


Fig. 3.

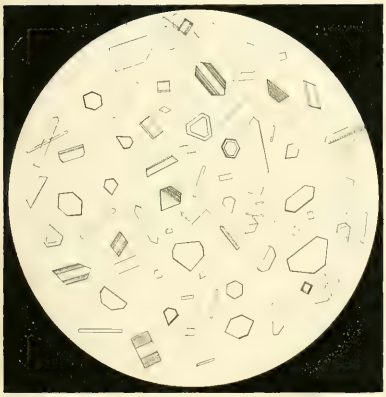


Fig. 4.

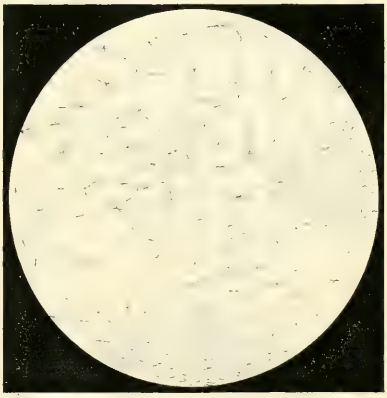


Fig. 5.

Fig. 6.

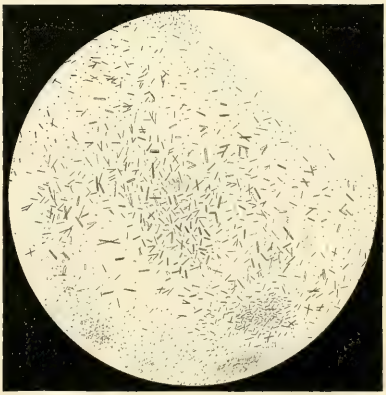


PLATE XVI.

APPARENT size of RED BLOOD CORPUSCLES under an amplification of 1150 diameters. The ACTUAL diameters of the corpuscles delineated are expressed in vulgar fractions of an inch, and as the numerator is always one, this is omitted in the illustration, thus: $3250 = \frac{1}{3250}$ of an inch.

FIG. 1. Blood-Corpuscles of Man, × 1150 diameters; average $\frac{1}{3250}$ inch.
" 2. " " " Dog, × " " " $\frac{1}{3561}$ "
" 3. " " " Mouse, × " " " $\frac{1}{3743}$ "
" 4. " " " Ox, × " " " $\frac{1}{4119}$ "
" 5. " " " Sheep, × " " " $\frac{1}{4870}$ "
" 6. " " " Goat, × " " " $\frac{1}{6189}$ "

Blood Corpuscles.

Fig. 1. Human.

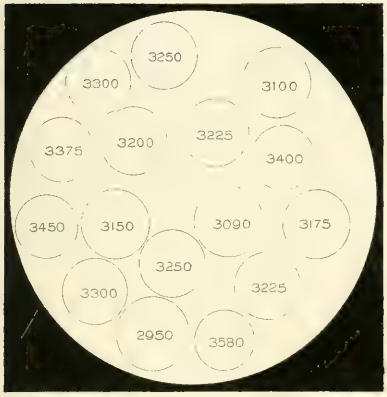


Fig. 2. Dog.

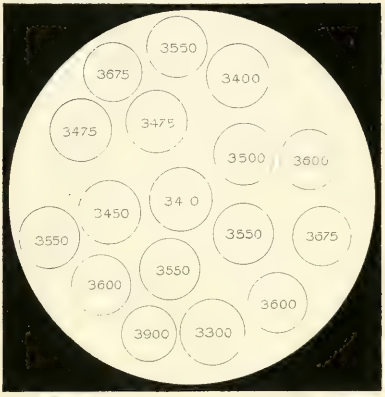


Fig. 3. Mouse

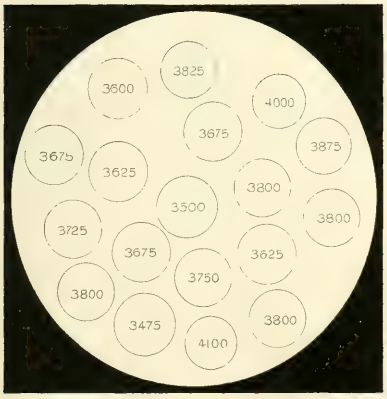


Fig. 4. Ox.

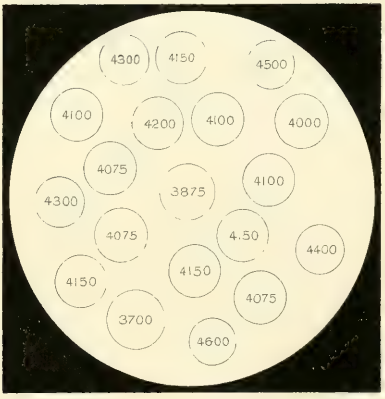


Fig. 5. Sheep.

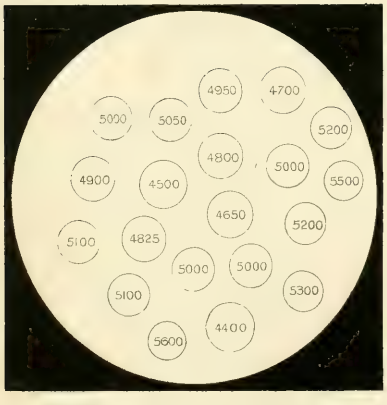
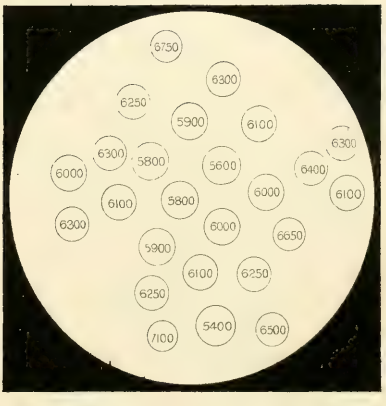


Fig. 6. Goat.



Mrs. J. Marshall &c.

TABULAR VIEW OF THE BEHAVIOR OF CERTAIN ALKALOIDS WITH REAGENTS.

ALKALOIDS	IN THE SOLID STATE					IN THE STATE OF AQUEOUS SOLUTION												SOLUBILITY
	1 Sulphuric Acid	2 Nitric Acid	3 Sulphuric Acid and Potassium Dichromate	4 Sulphuric Acid and Potassium Nitrate	5 Nitric Acid and Stannous Chloride	1 Potassium Hydrate and Ammonia	2 Potassium Iodide	3 Potassium Sulphocyanide	4 Potassium Chromate	5 Potassium Dichromate	6 Picric Acid	7 Auric Chloride	8 Platinic Chloride	9 Mercuric Chloride	10 Potassium Ferrocyanide	11 Potassium Ferricyanide	12 Iodine or Potassio-Iodide	13 Bromine or Bromo-Hydric Acid	
1 NICOTINE, $C_{10}H_{14}N_2$																		
2 CONIINE, $C_8H_{17}N$																		
3 MORPHINE $C_{17}H_{19}NO_3$																		
4 NARCOTINE $C_{22}H_{23}NO_7$																		
5 CODEINE $C_{18}H_{21}NO_3$																		
6 NARCEINE, $C_{23}H_{29}NO_9$																		
7 OPIANYL $C_{22}H_{23}NO_9$																		
8 STRYCHNINE, $C_{21}H_{22}N_2O_2$																		
9 BRUCINE, $C_{23}H_{26}N_2O_4$																		
10 ACONITINE, $C_{33}H_{45}NO_{12}$																		
11 ATROPINE and DATURINE $C_{17}H_{23}NO_3$																		
12 VERATRINE $C_{32}H_{49}NO_9$																		
13 JERVINE $C_{26}H_{37}NO_3$																		
14 SOLANINE, $C_{21}H_{35}NO_{15}$																		
15 GELSEMINE, $C_{20}H_{22}N_2O_2$																		

* The reactions in all instances, unless otherwise indicated, refer to the behavior of the alkaloid in the solid state. Where there is no reaction, as expressed, it is usually understood that the substance remains unchanged in color and character. The terms "soluble" and "insoluble" are relative, and refer to the behavior of the substance in water at the ordinary temperature of the air.

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THE END.